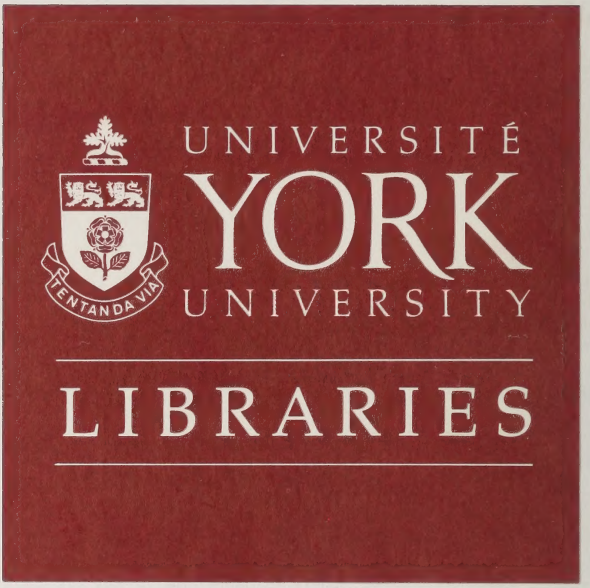
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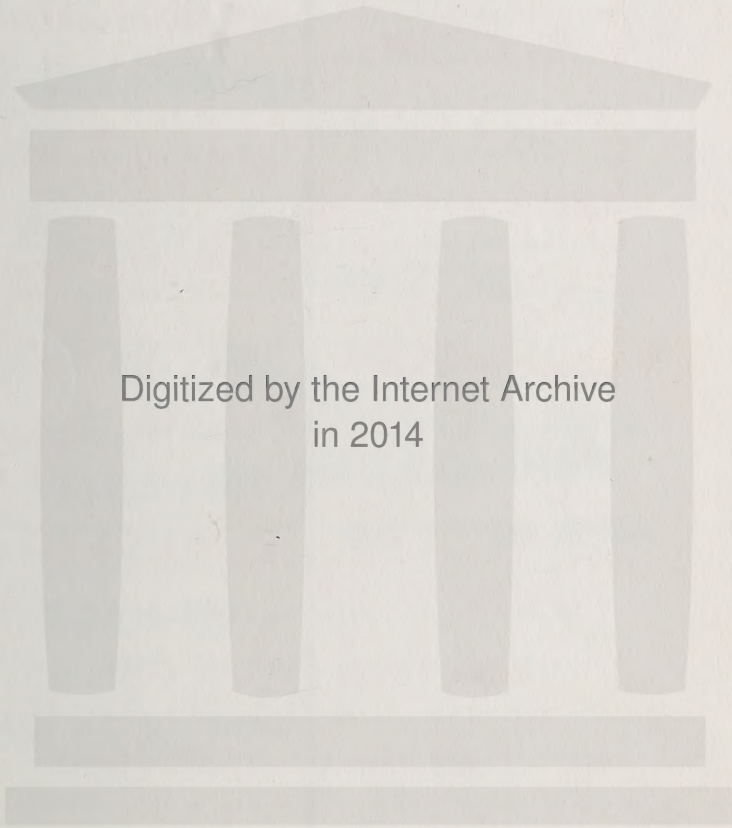
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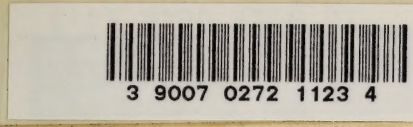
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THE SYNTHETIC DYESTUFFS AND THE INTERMEDIATE PRODUCTS FROM WHICH THEY ARE DERIVED.

BY

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EDITOR OF THE JOURNAL OF THE CHEMICAL SOCIETY; LATE MEMBER OF THE TECHNICAL COMMITTEE, BRITISH DYES, LTD., AND CHIEF CHEMIST, DALTON WORKS, HUDDERSFIELD; EXAMINER IN COAL TAR COLOURING MATTERS TO THE CITY AND GUILDS OF LONDON INSTITUTE,

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PREFACE TO FOURTH EDITION.

Although little advance has been made in the domain of dyes and their intermediate products since the last edition of this book was published, yet it has, the authors hope, been improved in certain directions. Due notice has been taken of the manufacture in England of various dyes formerly exclusively produced on the Continent, and it is thought that the brief description of the equipment of a technical laboratory (p. 220 *et seq.*) will prove useful.

J. C. CAIN.
London.

J. F. THORPE.
London.

Reprinted
for Fifth Edition.

PREFACE.

This book is not intended to be an exhaustive treatise on the subject, but is designed to serve the purposes of a laboratory text-book for the use of students in the chemical laboratories of technical schools, and of colleges where technical subjects, connected with this branch of higher organic chemistry, are taught. It is also hoped that matter will be found in it of use to chemists employed in works dealing with the synthetic dyestuffs.

The need for such a book has been repeatedly pointed out to us by teachers who have control of laboratories where the usual course, only, of organic preparation is carried out, and who have realised the incompleteness of such a course.

It is hardly necessary to say that those students who wish to rise to a position of any importance as chemist in works where the organic dyestuffs are in any way used, must be thoroughly conversant with the ordinary facts of organic chemistry, and in this book we have assumed that such theoretical knowledge has been acquired.

With such grounding, we maintain that the average student can, without much trouble, master the main principles of the chemistry of the organic dyestuffs, the one most important point for him to remember being that it is not necessary for him to attempt the impossible task of remembering the technical name and constitution of every existing dyestuff.

Every dyestuff belongs to some group of organic compounds, the other members of which have analogous properties and analogous reactions; and if the student knows the reactions and characteristics of one member of the group, he will be able to infer, with certain reservations which he will learn by experience, the properties of the other members of the same group.

In the first part of this book, therefore, we give a detailed theoretical description of the intermediate products and the dyestuffs.

In the second part we have described the preparation of one or more typical members of each of the groups of the intermediate products and dyestuffs.

Methods of preparation are described and quantities are recommended which will enable the ordinary apparatus of the laboratory to be available, but the materials employed are only such as would be used by a chemist actually experimenting in a chemical works. Thus the use of ether is avoided except where absolutely necessary.

By this means we hope to enable the student to pass from the college laboratory to the laboratory of the works without that serious loss of time which he now often experiences before he can adapt himself to the totally different nature of his surroundings.

Preceding the portion of the book dealing with the preparation of the dyestuffs will be found a short description of experimental dyeing, in which will be found methods for producing quantitative dyeings on the fibre, in the laboratory.

The complex nature of many of the commercial dyestuffs renders any chemical analysis of them extremely uncertain, and for the most part manufacturers and others rely upon the comparative dye-trial for an appreciation of any product with which they may have to deal.

A knowledge therefore of the methods by which the various dyestuffs can be quantitatively fixed upon the fibres is essential to those who intend ultimately to work with them.

We have also described the various methods by which the value of any dyestuff may be determined in respect to its behaviour on the fibre, towards reagents, and towards conditions which it is liable subsequently to meet with, and these data should not only be found of use to chemists investigating the nature of any new commercial product, but also to the research chemist, who, by this means, will be enabled to estimate the value of any new product which he may have isolated.

In the preparations dealing with the raw materials and dyestuffs, the plan has been adopted of arranging so that each preparation is, as far as possible, a reduced facsimile of the corresponding preparation in the chemical works.

Certain of the intermediate products will have to be subsequently used in the preparation of the dyestuffs, and in cases where such raw materials are not in ordinary use and readily obtained, we have given instructions for preparing them on a sufficiently large scale, to enable the student to obtain enough of them for future use.

In the third part we deal with the identification and analysis of intermediate products and dyestuffs.

In this case, also, we have described the actual processes in use in the chemical works.

Many of these must necessarily be somewhat empirical, and we have only described those which, from our own experience, yield the most satisfactory results.

Some of them—as, for example, Knecht's process for the titration of azo-dyestuffs—have not, to our knowledge, yet been applied technically, but we have inserted them because we are of the opinion that they are certain to be used in this connection in the future.

The student will find by experience that the only means of obtaining a knowledge of the reactions of the dyestuffs, both in the solid form and upon the fibre, is to possess a thorough knowledge of their constitution, and that if

such knowledge is lacking no tables of reactions of whatever nature will be of any use.

Such knowledge can only be obtained by studying the theory of the subject, and investigating for himself the properties and reactions of one or two members of each group.

The need of chemists in works, connected with the dyeing industry, possessing means of ascertaining the purity and character of the products with which they have to deal, cannot surely be over-rated, and we hope that this book will enable students to gain an insight into, and a practical knowledge of, the processes adopted in commerce, which are not usually gained during a course of organic preparations under existing conditions.

Many of the tables and matters dealing with the application of the dyestuffs have been adapted from the excellent handbooks issued by the various German dye-works, especially those of the Farbwerke vorm Meister Lucius & Brüning, Höchst a/M., Messrs Leopold Cassella & Co., Frankfort a/M., and of the Actien Gesellschaft für Anilinfabrikation, Berlin.

We are also indebted to Miss L. Drey, of the Manchester University, for the careful manner in which she has repeated many of the preparations.

J. C. CAIN. J. F. THORPE.

MANCHESTER, *May* 1905.

THIS WORK CONSISTS OF THREE PARTS:

PART I.—*Theoretical.*—A Theoretical Description of the Intermediate Products and Dyestuffs.

PART II.—*Practical.*—Methods for Preparing the More Important Intermediate Products and Dyestuffs on the Laboratory Scale.

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ABBREVIATIONS.

E.P.,	English Patent.
A.P.,	American Patent.
D.P.,	German Patent.
F.P.,	French Patent.
Amer. Chem. J.,	*American Chemical Journal.*
Ann.,	*Annalen der Chemie und Pharmacie.*
A. Ch.,	*Annales de Chimie et de Physique.*
Ann. Chim. anal.,	*Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.*
Ber.,	*Berichte der deutschen chemischen Gesellschaft.*
Brit. A. Rep.,	*British Association for Advancement of Science Report.*
Chem. Zeit.,	*Chemiker Zeitung.*
Chem. Zeitsch.,	*Chemische Zeitschrift.*
Dingl. pol. J.,	*Dingler's Polytechnisches Journal.*
J.C.S.,	*Journal of the Chemical Society.*
J. Ind. Eng. Chem.,	*Journal of Industrial and Engineering Chemistry.*
J. prak. Chem.,	*Journal für praktische Chemie.*
J.S.C.I.,	*Journal of the Society of Chemical Industry.*
J. Soc. Dyers,	*Journal of the Society of Dyers and Colourists.*
Monatsh.,	*Monatshefte für Chemie.*
Rec. trav. chim.,	*Recueil des travaux chimique des Pays-Bas et de la Belgique.*
Zeit. angew. Chem.,	*Zeitschrift für angewandte Chemie.*
Zeit. Farb. Chem.,	*Zeitschrift für Farben und Textil-Chemie.*
later altered to—	
Zeit. Farbenind.,	*Zeitschrift für Farbenindustrie.*

NAMES OF FIRMS.

[A],	Aktien Gesellschaft für Anilinfabrikation, Berlin.
[B],	Badische Anilin und Soda Fabrik, Ludwigshafen a/Rhein.
[BK],	Leipziger Anilinfabrik. (Beyer & Kegel, Lindenau-Leipzig.)
[Bl],	The Basle Chemical Co.
[By],	Farbenfabriken vorm Fr. Bayer & Co., Elberfeld.
[C],	Leopold Cassella & Co., Frankfort a/Main.
[Cl Co.],	The Clayton Aniline Co., Ltd., Clayton, near Manchester.
[D],	Dahl & Co., Barmen.
[DH],	L. Durand, Huguenin & Co., Basle and Hüningen.
[G],	J. R. Geigy, Basle.
[H],	Read Holliday & Sons, Ltd. (since 1915, British Dyes, Ltd.), Huddersfield.
[I],	Société pour l'Industrie chimique (formerly Bindschedler & Busch), Basle.
[K],	Kalle & Co., Biebrich a/Rhein.
[KS],	Sandoz & Co., Basle (formerly Kern & Sandoz).
[L],	Farbwerk Mühlheim (formerly A. Leonhardt & Co., Mühlheim).
[Lev],	Levinstein, Ltd., Crumpsall Vale, Manchester.
[M],	Farbwerke vorm Meister Lucius & Brüning, Höchst a/Main.
[Mo],	Société chimique des Usines du Rhône (late Gilliard, Monnet, & Cartier)
[O],	K. Oehler, Offenbach a/Main.
[P],	Société Anonyme des Matières Colorantes de St Denis, Paris.
[Sch],	The Schöllkopf Aniline & Chemical Co., Buffalo, U.S.A.

SYNTHETIC DYESTUFFS.

PART I.—THEORETICAL.

§ 1.—*INTERMEDIATE PRODUCTS.*

CHAPTER I.

COAL-TAR: ITS OCCURRENCE AND PURIFICATION.[1]

Coal-tar is produced by the dry distillation of coal, and is therefore a bye-product in the manufacture of coal-gas.

Coal being a substance rich in carbon and poor in hydrogen, furnishes on dry distillation substances which belong almost exclusively to the aromatic series, and by far the larger proportion of the aromatic compounds used in the preparation of the artificial dyestuffs are either obtained directly from coal-tar, or are formed from intermediate products prepared from substances present in the tar.

For a considerable time after the discovery of coal-gas, the tar produced was considered merely as an encumbrance and was used mainly as a pigment or fuel.

The discovery by A. W. Hofmann, in 1845, that the hydrocarbon benzene was present in the tar, caused his pupil Mansfield to work out a method for its commercial production. At that time, however, the first artificial dyestuff had not yet been prepared, and the enormous importance of this substance was not understood. It was not until the discovery of Mauveine in 1856 and of Fuchsine (Magenta) in 1859, both of which were indirectly prepared from benzene, that any considerable attempt was made to separate the tar into its various constituents.

The composition of tar varies very greatly according to the temperature of distillation.

The products from coal distilled at a low temperature, say 400° to 450° C., will consist chiefly of members of the paraffin and olefine series. The lower members of these series are liquids and the higher ones solid, so that coal distilled at a low temperature will yield comparatively little permanent gas. As the temperature of distillation is raised the paraffin hydrocarbons are destroyed, and benzenoid hydrocarbons, free carbon, and an increased production of permanent gas formed.

The usual temperature obtained in actual practice is from 980° to 1100° C., at which temperature there is a maximum yield of benzene, toluene, phenol, etc., in the tar, with a maximum of illuminating power in the gas.

[1] See books by Lunge and by Warnes (p. 208).

Should the temperature be taken beyond this there will be a larger production of gas at the expense of its light-giving constituents.

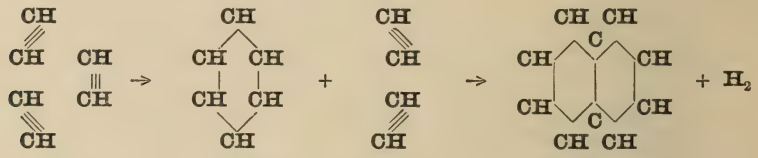
The tar also that is produced at a very high temperature contains a large percentage of naphthalene, phenanthrene, pyrene, etc., and a correspondingly diminished quantity of benzene, etc. (Newbigging, *Handbook for Gas Engineers and Managers*, 1904.)

This variation in the composition of coal-tar can be readily understood when the researches of Berthelot, Anschütz, and others on the polymerisation of hydrocarbons are taken into account.

Thus Berthelot, on passing hydrocarbons through red-hot tubes, found that aromatic compounds were produced from hydrocarbons of the aliphatic series by polymerisation and loss of hydrogen. In this way—

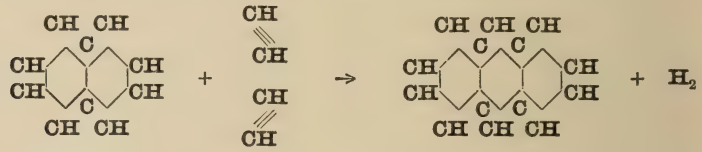
(1) Methane can be converted into propylene, benzene, and naphthalene.
(2) Acetylene can be converted into hydrogen, ethane, ethylene, benzene, styrene, and naphthalene.
(3) Benzene + ethylene can be converted into styrene, naphthalene, anthracene, etc.

The following scheme shows this :—



(Berthelot, *A. Ch.*, [4], ix. 469.)

Anthracene can also be formed from naphthalene and acetylene :—



The purification of coal-tar is effected by distillation. The crude tar, which contains a considerable quantity of ammonia water, is first freed from this by gravitation. It is then transferred to the stills, which are vertical, and connected with a worm surrounded with water, which can be either cooled or warmed as occasion requires.[1]

The tar in the stills is kept in motion by means of mechanical stirring apparatus, or by passing in a current of superheated steam.

The first operation consists in separating the distillate into the following parts :—

I. First runnings, up to 110° C.
II. Light oils, up to 210° C.
III. Carbolic oils, up to 240° C.
IV. Heavy or creosote oils, up to 270° C.
V. Anthracene oils, above 270° C.

[1] For a laboratory apparatus for distilling coal-tar see Kuhn, *Chem. Zent.*, 1906, i. 805.

The residue in the retort is run out and is known as "pitch."

From the "first runnings" and "light oils" benzene, toluene, and xylene are obtained; the "carbolic oils" yield phenol, cresol, and naphthalene; and the "anthracene oils" give anthracene.

The first runnings and light oils are fractionally distilled into three main fractions. The fraction of low boiling-point, containing acetonitrile, carbon disulphide, and fatty hydrocarbons, is removed, and the fraction of high boiling-point is mixed with the carbolic or creosote oils. The middle fraction is washed with caustic soda to remove phenols, then with strong sulphuric acid to remove bases, etc., and finally with water. The product, known as "crude benzol," is then fractionally distilled, and by this means separated into pure benzene, toluene, and xylene. The portion distilling after the xylene is used as "solvent naphtha."

Naphthalene crystallises out from the carbolic and heavy oils, and is separated by centrifuging and pressing. It is also deposited from the residues left in the still after distilling the first runnings and light oils. The crude naphthalene is washed with hot caustic soda solution to remove phenols, then with strong sulphuric acid to remove bases, and finally with very dilute caustic soda. It is then sublimed or distilled. (See *The Dyer*, 1917, xxxviii. 14.)

Anthracene is deposited from the anthracene oils as a green slimy mass, which is partially purified by pressing; in this state it contains about 12 to 14 per cent. of anthracene.[1]

There are a number of processes by which the crude anthracene may be purified sufficiently for conversion into anthraquinone, in which state it finds its most important application, namely, in the preparation of synthetic Alizarine.

I. The crude anthracene is extracted with solvent naphtha, which dissolves out the impurities and leaves a product containing about 40 per cent. of anthracene. This is usually not further purified, but is directly oxidised to anthraquinone, a process which causes the various impurities to be eliminated, thus—

(*a*) The crude anthracene contains other hydrocarbons, such as phenanthrene, fluorene, pyrene, etc., which on treatment with bichromate of potash and sulphuric acid remain for the most part unaltered, whilst the anthracene is oxidised completely to anthraquinone; on treating the oxidised mixture with moderately strong sulphuric acid the anthraquinone remains unaltered, but the hydrocarbons are converted into their sulphonic acids.

(*b*) On pouring the solution into water the sulphonic acids dissolve and the anthraquinone is deposited. This is finally purified by sublimation with superheated steam.

II. Another method consists in heating the crude anthracene with sulphurous acid, whereby the bulk of the impurities pass into solution and a product is left containing about 85 to 90 per cent. of anthracene.

III. Other solvents which have been found advantageous for this purpose are acetone oils and pyridine; by this last solvent a product containing from 95 to 98 per cent. of anthracene can be obtained.

Phenol is recovered from the alkaline washings of the various distillates on acidifying, for which purpose carbonic acid, in place of a mineral acid, has lately found a wide application.

The chief quantity of phenol is obtained from the "creosote oils," which form the intermediate, running between the light and the middle oils. It is purified by fractional distillation, the fractions of higher boiling-point, which contain cresols, being used for creosoting timber and for making disinfectants.

Altogether, nearly two hundred substances have been isolated from coal-tar. The average percentages of the more important are:—

[1] For an account of the manufacture of anthracene see Rispler, *Chem. Zeit.*, 1910, xxxiv. 1074, 1089.

	Average yield per cent. of the weight of tar.
Benzene,	0·6–0·8
Toluene,	0·2–0·4
Xylenes,	0·2–0·3
Phenols,	0·2–0·3
Cresols,	0·5–0·8
Naphthalene,	2–10
Anthracene,	0·2–0·4

The following is an analysis of a typical tar (Hooper, *J.S.C.I.*, 1910, xxix. 1438):—

	Per cent. by weight.				
Water (ammoniacal)	3·00				
Naphtha light oil	3·10	yields	1·0	per cent.	benzene.
Middle oil	7·68	„	1·5	„	toluene and solvent naphtha.
Creosote oil	10·15	„	8·12	„	naphthalene.
Anthracene oil	11·64	„	0·3	„	anthracene.
Pitch	61·00				
Loss	3·43				

Very considerable quantities of benzene and toluene are, at the present time, obtained from coke-oven gases. The gases contain as much as 42 grams per cubic metre of the hydrocarbons, and these are usually separated by scrubbing the gas with one of the higher boiling fractions of coal-tar.

The enormous importance of toluene and, in a less degree, of benzene at the present time has led to the elaboration of many other processes for the preparation of these compounds. It is stated, for example, that valuable results have been obtained by a process involving the "cracking" of petroleum in the presence of a catalyst.

CHAPTER II.

NITRATION. (*Benzene Series.*)

Speaking generally, the nitro-group (NO_2) is introduced into the aromatic nucleus by the direct action of nitric acid.

This action, which is characteristic of aromatic compounds, may be represented by the equation

$$C_6H_6 + NO_2OH \rightarrow C_6H_5NO_2 + H_2O,$$

the further action of nitric acid producing bodies containing two or more nitro-groups, according to the equation

$$C_6H_5NO_2 + NO_2OH \rightarrow C_6H_4(NO_2)_2 + H_2O.$$

Not only do the aromatic hydrocarbons yield nitro-derivatives, but also the many derivatives of these hydrocarbons made by substituting the hydrogen atoms by the hydroxyl (OH), amino (NH_2), aldehyde (CHO), carboxyl (COOH), etc., groups, the formation of the nitro-compound taking place with greater or less ease according to the nature of the substance nitrated.

Thus, in cases where the compound is very easily nitrated, the action of nitric acid diluted with water is sufficient to bring about the formation of the nitro-compound, whilst in other cases the presence of sulphuric acid is necessary before nitration can be effected.

In nitrating with nitric acid in the presence of sulphuric acid it is usually advisable to add the substance to be nitrated gradually to a well-cooled solution of nitric and sulphuric acids (*e.g.* naphthalene), although in special cases the reaction may be varied with advantage by dissolving the substance in concentrated sulphuric acid, and gradually adding the nitric acid to this solution (*e.g.* nitro-sulphonic acids), or also by adding the mixture of acids to the pure substance (*e.g.* benzene, etc.). In many cases nitration can be carried out by adding powdered sodium nitrate to the solution of the substance to be nitrated in sulphuric acid.[1]

On the large scale the operation is effected in a cast-iron pan fitted with a stirrer. The pan is so arranged that it can be cooled by a stream of cold water on the outside, as nitrations are usually carried on between 0° and 40°.

If the nitric acid or mixture of this with sulphuric acid is to be added to the substance contained in the pan, it is measured in a cast-iron or stoneware vessel placed at a convenient height above the pan. The product of nitration, which is generally in the liquid state, is allowed to settle, and separated from the "waste acid" by means of a tap at the bottom of the pan. If the substance nitrated is a sulphonic acid, the product is usually diluted with water and isolated by means of its calcium salt.

Reactions of the nitro-group.—The nitro-compounds of the hydrocarbons are indifferent neutral substances like the hydrocarbons themselves, but the entrance of the nitro-group into the aromatic nucleus, already containing either an acid or a basic group, modifies the reactions of these groups.

[1] See Grandmougin, *La technique moderne*, 5, [1], 217.

Thus phenol (C_6H_5OH), which is a sufficiently strong acid to form a stable sodium salt with caustic soda, but not acid enough to decompose carbonates, becomes, on conversion into trinitrophenol (picric acid), $C_6H_2(NO_2)_3OH$, a strong acid which readily reacts with carbonates. The same change is produced in the conversion of α-naphthol into Naphthol yellow (see page 47).

Conversely, aniline, $C_6H_5NH_2$, is converted on nitration into nitro-aniline, $C_6H_4(NO_2)NH_2$, a substance which is very much less basic than aniline itself.

One of the chief reactions of the nitro-group, and the one which causes it to be of so much importance in the preparation of dyestuffs and intermediate products, is its behaviour on reduction.

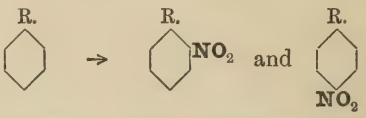
When treated with nascent hydrogen,[1] it is converted into the amino-group according to the scheme

$$R.\ NO_2 + 3H_2 \rightarrow R.\ NH_2 + 2H_2O.$$

(See p. 20.)

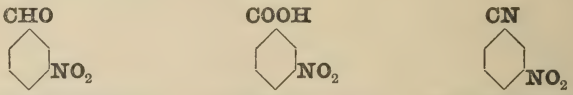
Orientation of the nitro-compounds.—Owing to the symmetrical nature of the benzene ring only one nitrobenzene is formed by the nitration of benzene.

When an alkyl group is present the nitro-group enters in the *ortho-* and *para-*, but not the *meta*-position. Thus—



The same position is taken up when the benzene ring contains an hydroxyl group. Thus *ortho-* and *para*-nitrophenol are formed by the nitration of phenol, $C_6H_5(OH)$.

When either the aldehyde (CHO), carboxyl (COOH), or cyanogen (CN) group is present in the benzene ring, the *meta*-nitro-compound is produced on nitration. Thus benzaldehyde (C_6H_5CHO), benzoic acid (C_6H_5COOH), and benzonitrile (C_6H_5CN) yield on nitration

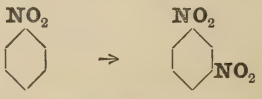


m-nitrobenzaldehyde, *m*-nitrobenzoic acid, *m*-nitrobenzonitrile,

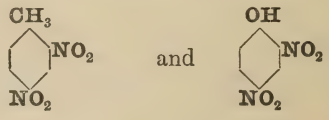
respectively.

The *meta*-position is also taken up when a benzene derivative already containing a nitro-group is further nitrated.

Thus nitrobenzene on further nitration yields *meta*-dinitrobenzene



and *ortho*-nitrotoluene and *ortho*-nitrophenol yield on nitration

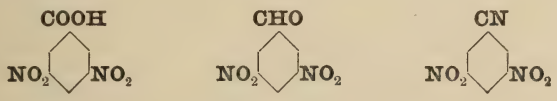


respectively.

[1] Under certain conditions other important reduction products are obtained, which will be described later.

Similarly, *meta*-nitro-compounds made by the nitration of compounds containing the groups COOH, CHO, or CN, yield on further nitration bodies containing the second nitro-group in the *meta*-position to the first.

Thus *m*-nitrobenzoic acid, *m*-nitrobenzaldehyde, and *m*-nitrobenzonitrile yield on further nitration



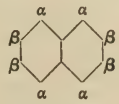
respectively.

NITRATION. (*Naphthalene Series.*)

The methods of introducing the nitro-group indicated in the case of the derivatives of benzene apply also to the naphthalene derivatives, and the reactions of the nitro-compound produced are the same.

A difference, however, arises in the orientation, owing to the asymmetric nature of the naphthalene molecule.

The constitution of naphthalene is represented by the formula



the two different positions in the nucleus which causes naphthalene to be capable of forming two mono-substitution products being represented by the signs (α) and (β) respectively.

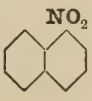
Another method is to number the positions in the manner indicated in the following formula :—

in which case the positions 2, 3, 6, 7, and 1, 4, 5, 8 become of equal value.

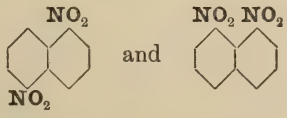
Orientation in the naphthalene series is shown in the table on p. 8 (*Reverdin* and *Fulda*).

By the nitration of naphthalene the α-position is occupied, and by further nitration the α-position 5 or 8.

Thus from naphthalene, α-nitronaphthalene is produced



which on further nitration passes into



1 : 5 1 : 8

If a hydrogen atom in naphthalene is replaced

by	Cl		Br		OH		OR		NO_2		NH_2		NHR		SO_3H		CN		COOH	
in the position	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
the new group	enters in the position																			
Cl	4		4		2 ?	1								1			5	5 or 8	5	
Br	4 5 or 8	? 5 or 8	4 5	8		1			5 or 8				4	1	5		5		5	
NO_2	4	8	4	8	2[1]	1[1]	2 4	1 6 or 7 8	5 8[2]		5 8	5 8	2 4	1	4 5 8	4 5 8	5 ?		5 8	5 8 ? ?
SO_3H under 100°	4 5	6 8	4 ?	6 8	2 4	6 8			5 6 7		4	5 8			5 6	5	5 ?		α β β	α
SO_3H above 100°	5	6			2	6 7					5 6	6 7				5 6 7				
NO					2 4	1														
COOH					2	1 3[3]														

[1] By means of NO_2. [2] At 60°, 1 : 3 is formed together with 1 : 5, not 1 : 8. [3] At higher temperatures.

CHAPTER III.

SULPHONATION. (*Benzene Series.*)

Aromatic compounds possess the characteristic property of forming sulphonic acids on treatment with strong sulphuric acid.

Thus benzene passes in this manner into benzene sulphonic acid,

$$C_6H_6 + OHSO_3H \rightarrow C_6H_5SO_3H + H_2O.$$

Aniline, on treatment with sulphuric acid, into aniline sulphonic acid (*p*-sulphanilic acid),

$$C_6H_5NH_2 + OHSO_3H \rightarrow C_6H_4(SO_3H)NH_2 + H_2O.$$

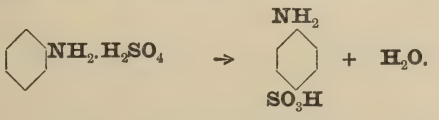
The sulphonic acid group is strongly negative, and on entering into the aromatic hydrocarbon converts it into a strong acid. Even when, as in sulphanilic acid, it enters into a nucleus already containing a basic group, its acid influence is such as to more than completely neutralise the basic influence of the amido-group, and thus sulphanilic acid exhibits acid properties.

The entrance of the sulphonic acid group is nearly always brought about by the action of sulphuric acid—the strength of the acid and the temperature of sulphonation depending on the nature of the substance, in some instances it being necessary to employ an acid containing a large percentage of free SO_3; occasionally also chloro-sulphonic acid is used; whilst in others even sodium bisulphite ($NaHSO_3$) has been found sufficient.

An interesting general method of introducing the sulphonic acid group is that described by Gattermann (*Ber.*, 1899, xxxii. 1136), which consists in preparing a sulphinic acid (SO_2H) by the action of finely divided copper on a diazo-solution which has been saturated with sulphur dioxide, and oxidising the product by means of alkaline permanganate.

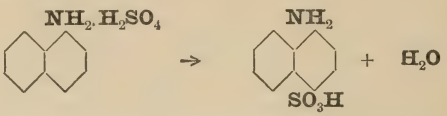
Another method, which has been applied more particularly to the preparation of the naphthalene polysulphonic acids, consists in oxidising the sulphur substitution compounds of the naphthalene sulphonic acids. These are obtained from the corresponding amido-compounds by treating the diazo-salt with potassium xanthate ($K(C_2H_5)CS_2O$) and hydrolysing the product with alkalies (E.P. 11,865[92]).

The so-called "baking process" for the introduction of the sulphonic acid group consists in roasting or baking the acid sulphate of a base. Thus, for example, aniline acid sulphate when heated to 180° undergoes an intramolecular change, and *p*-sulphanilic acid is quantitatively produced (see p. 232).



This process is also carried on technically for the manufacture of naphthionic acid from α-naphthylamine acid sulphate; but, unlike the above case, is difficult

to imitate on the small scale, so that the use of an excess of sulphuric acid is adopted in the example on p. 245.



The fact that the sulphonic acids are mostly soluble in water renders it necessary that some method should be adopted by which they can be separated from the excess of sulphuric acid used in the sulphonation.

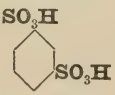
Here, again, special experimental methods have to be used in special cases. Those usually found most effective being—

(1) Precipitating the sulphonic acid from its solution by means of a saturated solution of some salt, such as sodium chloride, potassium chloride, etc.

(2) Treating the mixture of sulphuric acid and the sulphonic acid with either calcium, barium, or lead carbonates, and filtering. In many instances sulphonic acids form soluble salts with these metals which pass through in solution whilst the sulphates remain on the filter. The calcium salt is usually made on the large scale.

(3) In some cases the sulphonic acid is insoluble in cold sulphuric acid, and it is only necessary to filter the solution through asbestos or glass-wool in order to obtain it pure.

The orientation of the sulphonic acids is the same as that indicated in the case of the nitro-compounds. Thus benzene sulphonic acid on further sulphonation, is converted into *meta*-benzene disulphonic acid



Reactions.—The most important reaction of the sulphonic acid group is its conversion into the hydroxyl group (OH) on fusion with caustic soda.

Thus benzene sulphonic acid under these conditions is converted into phenol,

$$C_6H_5SO_3H + NaOH \rightarrow C_6H_5OH + NaHSO_3.$$

(See p. 28.)

Another important reaction, and one that is sometimes used in preparing compounds relating to the dyestuffs, is the production of the nitriles by fusing the sulphonic acid with potassium cyanide, thus:—

$$R.\ SO_3H + KCN \rightarrow R.\ CN + KHSO_3.$$

The introduction of the sulphonic acid group is also of considerable importance in the case of finished dyestuffs themselves, since, by its means, a dyestuff insoluble in water may be made soluble, and a soluble dyestuff more soluble. This, however, will be dealt with under its own head.

SULPHONATION. (*Naphthalene Series.*)

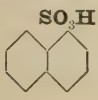
According to the law discovered by Armstrong and Wynne, the sulphonic acid group enters the α-position at low temperatures, but the β-position at high temperatures.

Thus on treating naphthalene with strong sulphuric acid at 80° C., α-naphthalene sulphonic acid

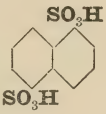
is produced; whilst at 180° C., β-naphthalene sulphonic acid is the chief product.[1]

The same law holds on further sulphonation. Thus the second sulphonic acid group enters the most remote α-position at low temperatures, and the most remote β-position at high temperatures.

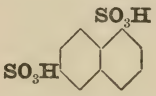
Thus the sulphonic acid



gives, on further sulphonation in the cold,



as chief product, and at higher temperatures the sulphonic acid

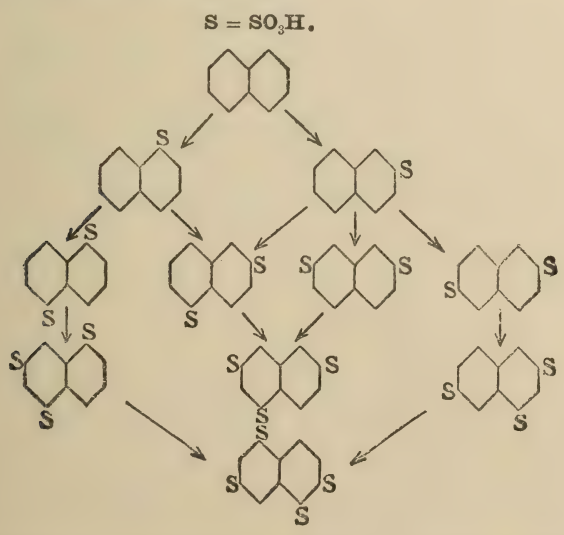


whilst the β-sulphonic acid gives, on further sulphonation at 160° C., the acids 2 : 6 and 2 : 7

and

as chief products.

The following scheme shows the production of the technically important sulphonic acids of naphthalene (*Heumann*) :—



[1] For the sulphonation of naphthalene see Euwes, *Rec. trav. chim.*, 1909, xxviii. 298, and Witt, *Ber.*, 1915, xlviii. 743.

The sulphonic acids of naphthalene are of considerable importance, since from them are produced the valuable naphthols on fusion with caustic soda.

Of much greater importance, however, are the various sulphonic acids derived from the naphthylamines and naphthols, made either by treating them directly with sulphuric acid or by indirect means.

These substances find an extensive application in the preparation of the azo-dyestuffs, and the special methods of preparation and the properties of the more important of them must therefore now be given.

Naphthylamine Sulphonic Acids.

These are obtained by the following general methods :—

(1) By sulphonating an amido-compound.
(2) By sulphonating a nitro-compound and subsequent reduction.
(3) By nitrating a sulphonic acid and subsequent reduction.

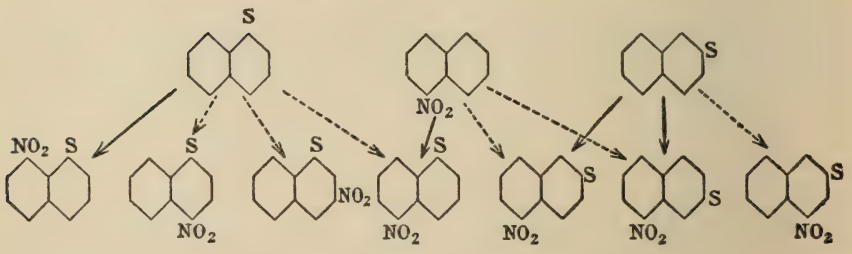
The last two methods will be first considered, and as the general operations of nitration and sulphonation have been already discussed, the different products formed are best explained by the following scheme (*Heumann*) :—

Chief product is represented by ——→

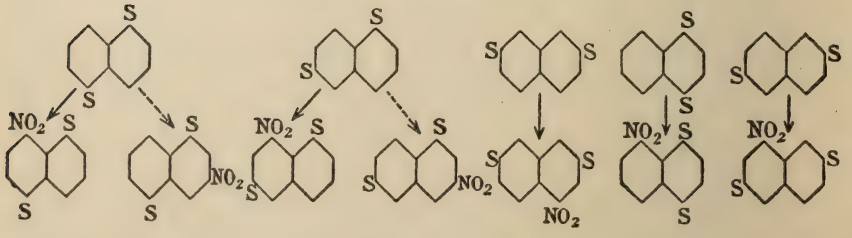
By-product is represented by ·····→

S = SO_3H.

Nitronaphthalene monosulphonic acids.

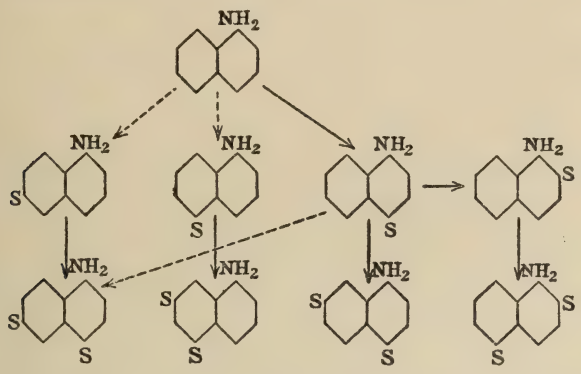


Nitronaphthalene disulphonic acids.

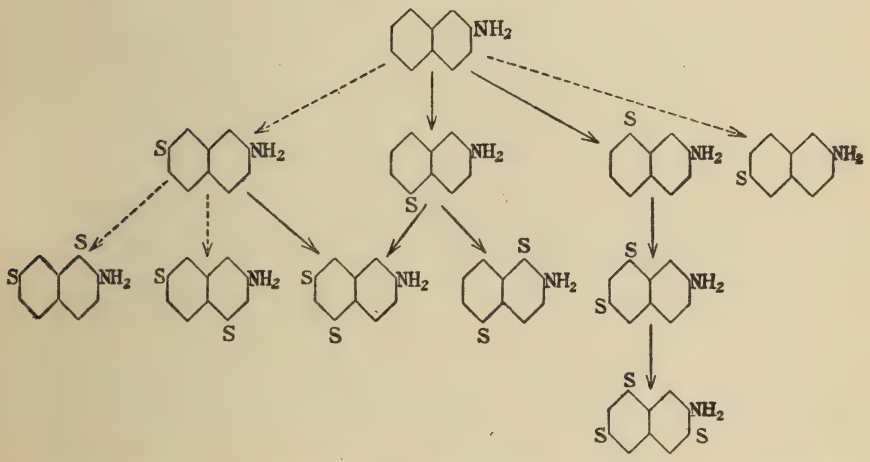


In carrying out the first method, both α- and β-naphthylamine are used on the large scale.

Scheme showing the sulphonic acids derived from α-naphthylamine by sulphonation (*Heumann*) :—

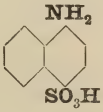


Sulphonic acids derived from β-naphthylamine by sulphonation (*Heumann*) :—



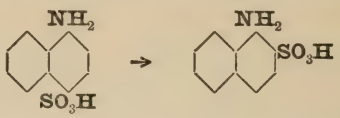
The following is a short description of the more important naphthylamine sulphonic acids; for a more detailed and complete description a larger work must be consulted (see Green, *Organic Colouring Matters*, 1904; Täuber and Norman, *Derivate des Naphtalins*, 1896, etc.) :—

Naphthionic acid



prepared on the large scale by roasting α-naphthylamine acid sulphate mixed with about 3 per cent. of its weight of oxalic acid, to 170–180°. The free acid is difficultly soluble in cold water, more easily in hot. The sodium salt "naphthionate" crystallises with four molecules of water. The diazo-compound is yellow and insoluble in water.

By heating the sodium salt with four parts of naphthalene, a molecular rearrangement takes place and "ortho-naphthionic acid" is formed



This acid is made on the large scale, but not to any great extent.

By the cold nitration of naphthalene α-sulphonic acid and subsequent reduction of the product, two acids are obtained, viz. :—

S (Schoellkopf) acid (α-naphthylamine sulphonic acid 1 : 8), and

L (Laurent) acid (α-naphthylamine sulphonic acid 1 : 5).

The 1 : 8 acid is the more important and is the chief product. The free acid is nearly insoluble in cold water.

When naphthalene β-sulphonic acid is nitrated and reduced, the three so-called "Cleve's" acids are obtained, viz., α-naphthylamine sulphonic acids 1 : 6, 1 : 7, and 1 : 3. The first two are formed in about equal proportions and form the bulk of the product, the last being present in traces only.

The reduction mixture is usually directly combined with diazo-compounds in the production of black polyazo-dyes for cotton (direct).

By salting out the reduction mixture, or acidifying, the 1 : 6 acid is precipitated. This gives rather better shades than the 1 : 7.

The more important of the monosulphonic acids of β-naphthylamine are the 2 : 6 and the 2 : 7 acids. The former (Brönner's acid) is obtained from "Schäffer's acid" (p. 16) by heating it with strong aqueous ammonia in an autoclave to 180°. The free acid is sparingly soluble in cold water; the sodium salt easily soluble.

The 2 : 7 or "F" acid is similarly obtained from the corresponding β-naphthol sulphonic acid (p. 16). This acid is more soluble in hot water than the preceding one, but its sodium salt is easily soluble in water.

Of the polysulphonic acids of the two naphthylamines, the following are of technical importance :—

1-Naphthylamine-3 : 6-disulphonic acid (Freund's acid).—Naphthalene-2 : 7-disulphonic acid is nitrated and the 1-nitronaphthalene-3 : 6-disulphonic acid produced is reduced with iron and hydrochloric acid. The acid is used for the preparation of wool blacks (azo-dyestuffs).

1-Naphthylamine-4 : 7-disulphonic acid (Dahl's No. III. acid). — When naphthionic acid is further sulphonated, a mixture of two disulphonic acids is obtained, viz., about 66 per cent. of the above acid and about 33 per cent. of the 1 : 4 : 6 acid (Dahl's No. II.). The latter is worthless for the preparation of azo-colouring matters; the former, however, is used in the preparation of wool blacks. The acid is easily soluble in hot water, sparingly soluble in cold.

1-Naphthylamine-4 : 8-disulphonic acid (δ or S acid).—This is prepared by treating 1-naphthylamine-8-sulphonic acid with fuming sulphuric acid, or together with 1-naphthylamine-3 : 8-disulphonic acid, by the nitration and reduction of the mixture of naphthalene-1 : 5-and-1 : 6-disulphonic acids obtained by sulphonating naphthalene with fuming sulphuric acid at the ordinary temperature.

2-Naphthylamine-3 : 6-disulphonic acid (amido R acid) is obtained by heating the corresponding naphthol acid with aqueous ammonia in an autoclave.

The acid is much used as a component with which diazo-compounds are

coupled to form azo-dyes, and it is also diazotised itself and combined with other components.

2-Naphthylamine-6 : 8-disulphonic acid (amido G acid) is obtained by heating the corresponding naphthol acid (G salt) with aqueous ammonia in an autoclave; also by sulphonating β-naphthylamine with fuming sulphuric acid (see p. 250).

The free acid is easily soluble in water.

Diazo-compounds do not combine with it. It is used, in the form of its diazo-compound, in the production of wool blacks.

This acid is also an important intermediate material in the manufacture of "γ" acid (amidonaphthol monosulphonic acid) (see p. 17).

1-Naphthylamine-3 : 6 : 8-trisulphonic acid.—The starting-point for this acid is naphthalene or sodium naphthalene-β-sulphonate. The material is heated with fuming sulphuric acid and the sulphonation mixture directly nitrated. The nitration mixture is reduced and the solution saturated with salt, when the disodium hydrogen salt is precipitated quantitatively; this, by melting with caustic soda, is converted into amidonaphthol disulphonic acid H (p. 18).[1]

1-Naphthylamine-4 : 6 : 8-trisulphonic acid is obtained by the nitration and reduction of naphthalene-1 : 3 : 5-trisulphonic acid.

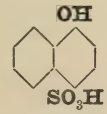
2-Naphthylamine-3 : 6 : 8-trisulphonic acid is obtained by heating 2-naphthol-3 : 6 : 8-trisulphonic acid with strong aqueous ammonia in an autoclave.

The acid is an important intermediate product in the manufacture of amidonaphthol disulphonic acid 2G (γ-disulphonic acid).

Naphthol Sulphonic Acids.

These acids are obtained either (1) by the sulphonation of naphthols, or (2) by converting naphthylamine- or chloronaphthalene-sulphonic acids or naphthalene polysulphonic acids into the corresponding naphthol sulphonic acid by treatment with nitrous acid and subsequent boiling of the diazo-compound, or by melting with caustic alkali.

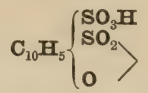
The most important of the α-naphthol sulphonic acids is the *1 : 4 acid*, or *Nevile and Winther's acid*,



This is prepared (1) by boiling the diazo-compound from naphthionic acid with dilute sulphuric acid; (2) by heating sodium naphthionate with 50 per cent. aqueous caustic soda in an autoclave; (3) by heating naphthionic acid with sodium bisulphite and decomposing the product with alkalies. The acid forms very soluble transparent tables. When prepared according to the first method, the solution is invariably coloured red from the formation of the azo-colour (diazotised naphthionic acid + N. and W. acid); and when prepared in this way the acid is usually not separated, but the solution used direct.

1-Naphthol-3 : 8-disulphonic acid (ε acid) is obtained by boiling the diazo-compound of the corresponding α-naphthylamine-3 : 8-disulphonic acid with dilute sulphuric acid; the product is the sultone-sulphonic acid

[1] 1-Naphthylamine-3 : 6 : 8-trisulphonic acid is also obtained by sulphonating naphthalene-2 : 7-disulphonic acid to 1 : 3 : 6-trisulphonic acid, with subsequent nitration and reduction.



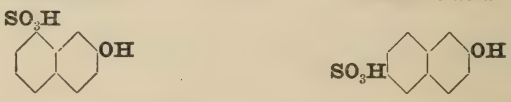
which is converted into the acid by dissolving in alkalies. This acid is also obtained by heating the acid sodium salt of the same naphthylamine-3 : 8-disulphonic acid with four parts of water to 180° in an autoclave. It is used as a component in the preparation of Erika B and Benzo-violet.

(α-Naphthylamine-3 : 8-disulphonic acid is obtained by nitration and reduction of naphthalene-1 : 6-disulphonic acid.)

β-Naphthol Sulphonic Acids.

By sulphonating β-naphthol with a small quantity (two parts) of concentrated sulphuric acid, a mixture of two monosulphonic acids is obtained, viz.,

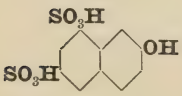
Crocein acid and Schäffer's acid



If the temperature be kept low the crocein acid predominates, but at a higher temperature Schäffer's acid is produced in the greater quantity. If the amount of sulphuric acid is increased, *di*sulphonic acids are formed, and here again the quantity of one or the other varies according to the temperature at which the sulphonation is carried out.

At a low temperature we have chiefly

G acid



and at a higher temperature chiefly R acid

A small amount of Schäffer's acid is also formed. G acid thus results from further sulphonation of crocein acid, and R acid from Schäffer's acid. In their chemical behaviour the crocein acid and G acid correspond to each other, as do also the Schäffer's and R acid.

Thus the former pair combine with much greater difficulty with diazo-compounds than do the latter; they are also much more easily soluble in water, salt solution, and alcohol than the latter, and the methods of separation of these acids from each other depend on one or other of these differences.

When combined with diazo-compounds, crocein acid and G acid yield yellow shades (hence the name for the latter, *gelb* = yellow), and Schäffer's acid and R acid yield red shades (*rot* = red).

By further sulphonation of either G or R acid *2-naphthol-3 : 6 : 8-trisulphonic acid* is obtained.

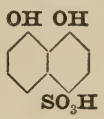
The second method of preparation of naphthol sulphonic acids is adopted in the case of *2-naphthol-7-sulphonic acid* (F acid), which is obtained by heating naphthalene-2 : 7-disulphonic acid (sulphonation of naphthalene-β-sulphonic acid) with caustic soda. By carefully regulating the quantities and temperature, only one sulphonic acid group is attacked. At a higher temperature 2 : 7-dihydroxynaphthalene is obtained.

The foregoing naphthylamine- and naphthol-sulphonic acids are often treated further in order to obtain still more valuable products for the production of dyes.

On melting a naphthylamine- or naphthol-di- or tri-sulphonic acid with caustic soda, one sulphonic acid group, as a rule, is attacked (under the special conditions of temperature, etc.), and an amidonaphthol- or dihydroxynaphthalene-mono- or disulphonic acid results.

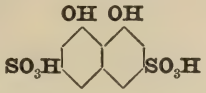
The following are the principal acids of this group :—

1 : 8-Dihydroxynaphthalene-4-monosulphonic acid (S)



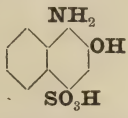
is prepared by melting α-naphthol-4 : 8-disulphonic acid (prepared from α-naphthylamine-4 : 8-disulphonic acid by boiling the diazo-compound with dilute acid) with caustic soda, or by heating 1 : 8-diamidonaphthalene-4-sulphonic acid with milk of lime under pressure. The acid is used for preparing azo-dyestuffs.

1 : 8-Dihydroxynaphthalene-3 : 6-disulphonic acid (chromotrope acid)



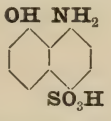
is prepared by melting α-naphthol-3 : 6 : 8-trisulphonic acid with caustic soda; also by heating α-naphthylamine-3 : 6 : 8-trisulphonic acid or 1 : 8-amidonaphthol-3 : 6-disulphonic acid with caustic soda solution; or thirdly, by heating 1 : 8-diamidonaphthalene-3 : 6-disulphonic acid with dilute acids or alkalies. The acid is employed in the manufacture of the important chromotrope azo-dyestuffs.

1 : 2-Amidonaphthol-4-monosulphonic acid



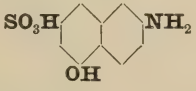
is prepared by treating nitroso-β-naphthol with sodium bisulphite.

1 : 8-Amidonaphthol-4-monosulphonic acid (S acid)



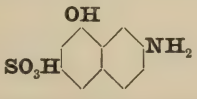
prepared by melting 1-naphthylamine-4 : 8-disulphonic acid (p. 14) with caustic soda. The acid is much used in the production of blue azo-dyes.

2 : 5-Amidonaphthol-7-monosulphonic acid (J acid)



is prepared by melting 2-naphthylamine-5 : 7-disulphonic acid with caustic soda.

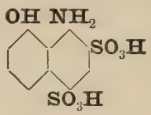
2 : 8-Amidonaphthol-6-monosulphonic acid (γ acid),



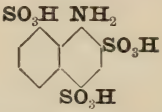
This, perhaps the most important of the whole of the sulphonic acids derived from

naphthalene, is prepared by melting 2-naphthylamine-6 : 8-disulphonic acid (p. 15) with caustic soda in an autoclave (see also p. 250).

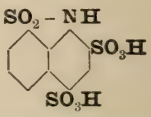
1 : 8-Amidonaphthol-2 : 4-disulphonic acid (2S acid)



is obtained by melting 1-naphthylamine-2 : 4 : 8-trisulphonic acid

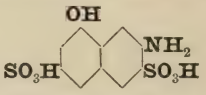


or its anhydride



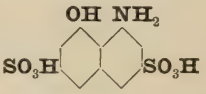
(prepared by further sulphonation of α-naphthylamine-8-sulphonic acid or -4 : 8-disulphonic acid) with caustic soda. It is used especially for making bright blue azo-dyes for cotton.

2 : 8-Amidonaphthol-3 : 6-disulphonic acid (2R acid)

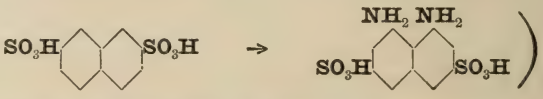


is obtained by melting 2-naphthylamine-3 : 6 : 8-trisulphonic acid (p. 15) with alkalies. The acid is used for making black colours dyeing cotton direct.

1 : 8-Amidonaphthol-3 : 6-disulphonic acid (H acid)

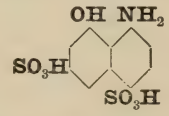


is prepared by melting 1-naphthylamine-3 : 6 : 8-trisulphonic acid with caustic soda. Also from 1 : 8-diamidonaphthalene-3 : 6-disulphonic acid (prepared by dinitration and reduction of naphthalene-2 : 7-disulphonic acid



by heating with dilute sulphuric acid under pressure.

1 : 8-Amidonaphthol-4 : 6-disulphonic acid (K acid)

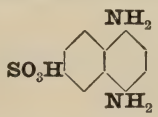


is prepared by melting 1-naphthylamine-4 : 6 : 8-trisulphonic acid with caustic soda. The latter is obtained by nitration and reduction of naphthalene-1 : 3 : 5-trisulphonic acid, which is produced on further sulphonating naphthalene-1 : 5-disulphonic acid. 1 : 8-Amidonaphthol-4 : 6-disulphonic acid, like the preceding acid (H acid), is much used for the manufacture of blue azo-dyes for cotton.

By the introduction of a second amido-group into a naphthylamine sulphonic acid, diamidonaphthalene sulphonic acids are obtained.

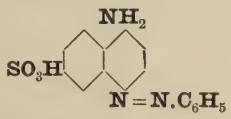
This is brought about by either (1) nitration and reduction of the naphthylamine sulphonic acid, the amido-group having been protected by conversion into the acetamido-group ; or (2) combining a diazo-compound with the acid and reducing the azo-colouring matter formed.

1 : 4-Diamidonaphthalene-6-monosulphonic acid



is obtained (as monoacetyl compound) from the 1 : 6 or 1 : 7-naphthylamine sulphonic acid (Cleve's acids) or a mixture of the two by nitrating the acetyl compound and reducing (with iron and *acetic* acid) the nitro-acid.

Another method is to combine the acids or mixture of acids with diazobenzene chloride forming the azo-dye



and then to reduce this, whereby the diamido-acid is produced and the other product of reduction—viz. aniline—removed by steam distillation.

The diamido-acid is converted into the monoacetyl compound by boiling with acetic acid.

In order to diazotise this acid, it is necessary to perform the operation in two steps, as the two amido-groups cannot be diazotised at the same time. For this reason, one is protected by acetylation, and then the other can be converted quantitatively into the diazo-group. After this has been combined with a component, the resulting substance is hydrolysed, and the second amido-group can now be successfully diazotised and combined with a suitable component.

Azo-colours formed in this manner with the above acid belong to the Diaminogen class.

CHAPTER IV.

AMIDO-COMPOUNDS (NH_2). (*Benzene Series.*)

Monamines.

The introduction of the amido-group is usually brought about by the reduction of the nitro-group according to the equation

$$R.\ NO_2 + 3H_2 \rightarrow R.\ NH_2 + 2H_2O.$$

Practically any acid-reducing agent may be used for this purpose, and it is usual on the laboratory scale to employ tin and hydrochloric acid; but owing to its cheapness iron generally replaces the tin technically.

Furthermore, the use of iron has another advantage, since, by its means, considerably less (about $\frac{1}{40}$) hydrochloric acid than that theoretically required can be used.

This is explained by the following equations (Raikow, *Zeit. angew. Chem.*, 1916, xxix., i. 196, 239):—

$$R.\ NO_2 + 3Fe + 6HCl \rightarrow 3FeCl_2 + 2H_2O + R.\ NH_2.$$

$$2\ R.\ NH_2 + FeCl_2 + 2H_2O = 2\ R.\ NH_2,HCl + Fe(OH)_2.$$

$$2\ R.\ NH_2,HCl + Fe = 2\ R.\ NH_2 + FeCl_2 + 2H.$$

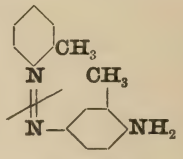
This theory, involving the idea of the hydrolytic decomposition of the ferrous chloride, is confirmed by the fact that the addition of salts such as magnesium chloride to a mixture of iron, water, and nitrobenzene, effects the reduction.

Nitro-compounds are also reduced by means of sodium bisulphite, in which reaction a sulphonic acid is often produced; thus *m*-dinitrobenzene gives nitraniline sulphonic acid. In certain cases sodium sulphide is used as reducing agent (see p. 24).

Another method of introducing the amido-group, and one frequently employed, consists in reducing an azo-compound.

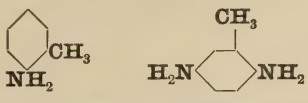
A good instance of this, and one which serves to explain the process, is the following:—

o-Toluidine is a bye-product in the manufacture of Magenta, and on treatment with nitrous acid in the presence of a small quantity of mineral acid is converted into amidoazotoluene



which, on reduction, splits up in the manner indicated by the line, giving a

mixture of *o*-toluidine and *p*-toluylenediamine



The mixture of these two bases is subsequently used in the preparation of Safranine (see p. 291).

An altogether different method is one which has been proposed for the preparation of *p*-nitraniline (Clayton Aniline Co. ; E.P. 24,869[02]).

This consists in heating *p*-chloronitrobenzene with excess of aqueous ammonia at 130–180°.

Diamines.

The chief diamines of the benzene series which are used in the manufacture of dyestuffs are *m*-phenylenediamine, *m*-toluylenediamine, and *p*-phenylenediamine (in the form of its monoacetyl derivative).

The meta-diamines are used chiefly as components in the preparation of azo-dyes and Bismarck brown, while the para-derivative is used as a diazo- (or tetrazo-) compound.

Both *m*-phenylene and *m*-toluylenediamine are obtained by the reduction of the corresponding dinitro-compounds with iron and a little hydrochloric acid. Nitrous acid converts them into Bismarck brown, although by acting on *m*-phenylenediamine with nitrous acid, which is added to it suddenly, nitroso-*m*-phenylenediamine is formed as well as Bismarck brown (Täuber and Walder, *Ber.*, 1900, xxxiii. 2116).

As *p*-phenylenediamine itself cannot be satisfactorily diazotised, it is usually prepared in the form of its monoacetyl compound by reduction of *p*-nitracetanilide with iron borings and acetic acid (see example, p. 231). The amidoacetanilide or acetyl-*p*-phenylenediamine is easily and quantitatively diazotised, and may be coupled with any component. If now the product be heated with alkalies, the acetyl group is split off, and the second amido-group may now, in like manner, be converted into the diazo-group. Another way of producing the same end-product, although not so conveniently carried out, is to start from *p*-nitraniline and to diazotise it and couple with a component. The product is now reduced carefully (so as to leave the azo-group $-N=N-$ unattacked) with sodium sulphide, and the resulting amido-group diazotised as before.[1]

A most important class of diamines is that belonging to the diphenyl series, for a large number of these when tetrazotised and coupled with suitable components yield dyestuffs capable of dyeing unmordanted cotton direct. This property is, indeed, not confined to the diphenyl derivatives, but is possessed by *p*-phenylenediamine itself, and by diamines of the diphenylamine series and others.

The simplest member of this group is *p-p*-diamidodiphenyl or *benzidine*

[1] For the manufacture of *p*-phenylenediamine see Jansen, *Zeit. Farbenind.*, xii. 197 ; *Chem. Zeitsch.*, xii. 109.

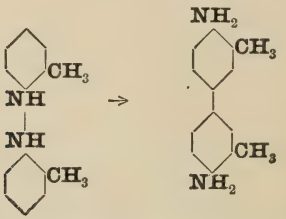
This is prepared by the alkaline reduction (Zn and NaOH) of nitrobenzene by which hydrazobenzene, $C_6H_5NH-NHC_6H_5$, is obtained, and then by treatment with cold hydrochloric acid a remarkable molecular change takes place, whereby benzidine is produced,

$$C_6H_5NH-NHC_6H_5 \rightarrow NH_2.C_6H_4.C_6H_4.NH_2.$$

The reduction to hydrazobenzene has also been brought about of late years electrolytically. (See Elbs, *Electrolytic Preparations*, 1903; F. M. Perkin, *Practical Methods of Electrochemistry*, 1905.)

By subjecting *o*-nitrotoluene to the same process (alkaline or electrolytic reduction), hydrazotoluene is produced, which is, in like manner, by the action of acids, transformed into *p-p*-diamidoditolyl or *tolidine*

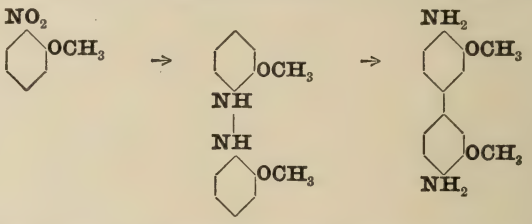
and



This base gives azo-colouring matters very similar in dyeing properties to benzidine.

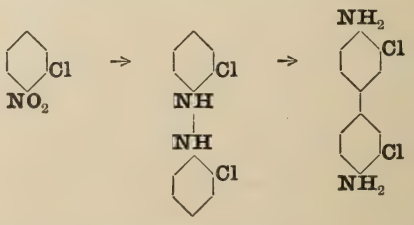
Other bases are:—

Dianisidine, obtained in an exactly similar way to tolidine from *o*-nitroanisol,



This base gives azo-dyes which dye cotton a much bluer shade than the above bases.[1]

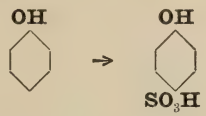
Dichlorobenzidine, obtained by chlorination and subsequent saponification of diacetylbenzidine, and also by the above-described process, from *o*-nitrochlorobenzene



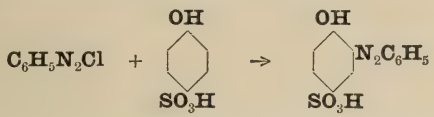
The only example of an unsymmetric base which is used on the large scale is *ethoxybenzidine*, which is obtained as follows:—

[1] For the manufacture of dianisidine see Jansen, *Zeit. Farbenind.*, xii. 247; *Chem. Zeitsch.*, xii. 171.

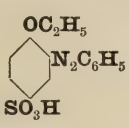
(1) Phenol is sulphonated to the *p*-sulphonic acid



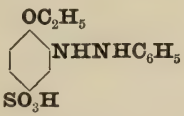
(2) diazobenzene chloride is combined with this



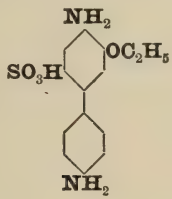
and (3) the product is ethylated, yielding benzeneazophenetol sulphonic acid



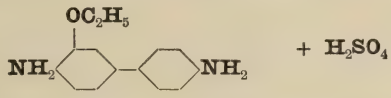
This by alkaline reduction yields the hydrazo-compound



and, with acids, ethoxybenzidine monosulphonic acid



which, on heating with water to 170° C., yields ethoxybenzidine



Reactions of the amido-group.—The property possessed by the aromatic amines of giving diazo-chlorides when their hydrochlorides are treated with nitrous acid causes them to be of considerable importance in the dyeing industry, not only because of the fact that these diazo-chlorides are the basis of the azo-dyes, but also because from them a number of important derivatives of the hydrocarbons can be formed.

The diazo-chlorides are prepared by the action of nitrous acid on the hydrochloride of the amine in the cold according to the equation

$$\text{R. } NH_2HCl + NOOH \rightarrow \text{R. } N_2Cl + 2H_2O,$$

and will be fully dealt with later.

The following reactions of these diazo-salts are important:—

(1) R. $N_2Cl + H_2O$ (hot) → R. $OH + HCl + N_2$.

(2) R. N_2I —(on heating)→ R. $I + N_2$.

(3) R. $N_2Cl + C_2H_5OH$ → R. $OC_2H_5 + HCl + N_2$.
or R. $N_2Cl + C_2H_5OH$ → R. $H + N_2 + CH_3CHO + HCl$.

(4) R. N_2Cl → R. $Cl + N_2$.
(5) R. N_2Br → R. $Br - N_2$.
(6) R. N_2CN → R. $CN + N_2$.
} In the presence of the corresponding cuprous salt.

Reactions 4, 5, and 6 are known as the Sandmeyer reactions, and are of general application.

The amido-compounds may be converted into nitro-compounds on nitration, or into sulphonic acids on sulphonation.

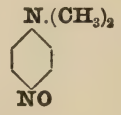
Thus aniline, $C_6H_5NH_2$, on nitration as acetanilide, $C_6H_5NH.COCH_3$, yields *o*- and *p*-nitracetanilide, which give the corresponding nitranilines on hydrolysis.

By nitrating benzylideneaniline, $C_6H_5N : CHC_6H_5$, the para-derivative is almost exclusively formed. *m*-nitraniline is produced from *m*-dinitrobenzene by reduction with a mixture of sodium sulphide and sulphur.

The most important sulphonic acid of aniline is the para-compound

and this is prepared by the direct treatment of aniline with sulphuric acid, or, better, by the action of heat on aniline acid sulphate (see p. 232).

By the action of methyl alcohol and sulphuric acid on aniline, the important dimethylaniline $C_6H_5N(CH_3)_2$ is produced, which on treatment with nitrous acid is converted into *p*-nitrosodimethylaniline



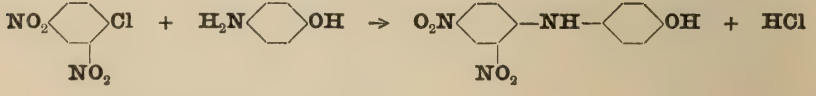
largely used in the preparation of dyestuffs.

The considerable importance which has recently been acquired by those sulphur colours which are prepared from diphenylamine and its derivatives causes this substance to be of great technical interest.

Diphenylamine is prepared by heating aniline with aniline hydrochloride under pressure,

$$C_6H_5NH_2,HCl + C_6H_5NH_2 \rightarrow C_6H_5NHC_6H_5 + NH_4Cl,$$

and derivatives of it may be prepared by heating together any nitro-compound containing a halogen atom in the ortho-position to the nitro-group with a primary amine in the presence of sodium acetate, thus

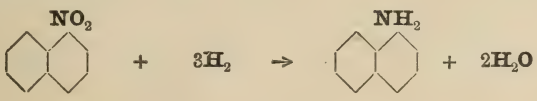


AMIDO-COMPOUNDS (NH_2). (*Naphthalene Series.*)

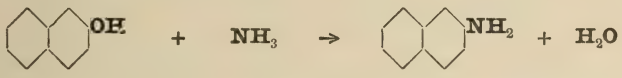
The remarks already made concerning the formation of the amido-compounds of the benzene series apply also to the derivatives of naphthalene.

Since by the nitration of naphthalene only α-derivatives are formed, α-naphthylamines alone can be formed by their reduction.

Thus α-nitronaphthalene yields α-naphthylamine,



β-naphthylamine must therefore be made by other means, and is formed by heating β-naphthol with ammonia,



Both these amines yield, on treatment with nitrous acid, diazo-salts which are of considerable importance in the dyeing industry.

Preparation of diazo-salts.—The preparation of solutions of diazo-salts on the small scale is fully described in the examples given on pp. 254-267, but there are a few points which may with advantage be indicated regarding the diazotisation of amines and diamines as carried out technically.

The first stage of the process consists in bringing the amine into solution, or at any rate into a finely divided state.

In the case of such substances as aniline, toluidine, etc., this is easily attained by adding the right quantity of hydrochloric acid and water. Solids, such as the naphthylamines, benzidine, tolidine, etc., are mixed with hot water at 50–60°, and easily dissolve on adding the calculated amount of hydrochloric acid. In the case of a few other substances, *e.g.* dianisidine, it is usual to take boiling water.

In many cases the addition of the further quantity of hydrochloric acid necessary for diazotisation produces a precipitate of the hydrochloride of the base (as a rule the hydrochloride is much more soluble than the sulphate, so that hydrochloric acid is generally used), and for this reason such addition is postponed till the solution has been cooled for the diazotising process. Addition of acid now precipitates the hydrochloride, but in a much more favourable condition for being acted upon by nitrous acid than if it were brought down while still hot.

In the case of aniline and bases, the hydrochlorides of which are easily soluble in water, the whole of the acid necessary may be added at once.

In whatever way the solution of the hydrochloride is prepared, it must be considerably cooled before conversion into the diazo-salt. Even in the preparation of diazo-salts which are very stable the solution must be cooled, in order to prevent the escape of nitrous acid.

Generally speaking, when diazo-salts are relatively unstable, *e.g.* the diazo-chlorides of benzene, toluene, xylene, etc., the solution should be cooled to 0° C. and not allowed to rise above 4–5° C. A considerable amount of heat is evolved when the sodium nitrite is run into the acid solution, so that lumps of ice should always be present during the process. In the case of more stable salts, such as the diazo-chlorides prepared from benzidine, tolidine, dianisidine, etc., the

starting temperature may be 8–10° C., and the final point 15° C.[1] The amount of hydrochloric acid which is necessary for diazotisation is, according to the equation

$$X.\ NH_2 + 2HCl + NaNO_2 = X.\ N_2Cl + NaCl + 2H_2O,$$

two molecules to one of the base. A considerable excess of this quantity is, however, taken in practice, as otherwise a diazoamido-compound is formed. The usual quantity is two and a half to three molecules to one of the base (or NH_2 group), but occasionally six or seven molecules of acid are necessary to prevent the formation of the precipitate of diazoamido-compound (as in the case of *p*-nitraniline). The actual diazotising process is very simple; it only consists in running in a solution of the calculated quantity of sodium nitrite till a reaction is obtained with iodide-starch paper after the solution has been stirred for five to ten minutes. The diazo-solution should be quite clear and free from foam.

In certain cases where an insoluble base has to be diazotised, it is usually stirred for a long time with acid and excess of nitrite solution till the diazotisation is complete. This is not, of course, ascertained by the use of test paper, but by observing the change of colour, solubility, etc., of the substance under treatment.

The diazo-compound is then usually coupled with a component, as in the preparation of azo-dyes; or is added slowly to a boiling solution of sulphuric acid (in the decomposition of the diazo-salt prepared from naphthionic acid, the filtered yellow diazo-compound is stirred up with water before running into the hot acid), in order to replace the group N_2Cl by the OH group.

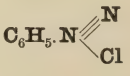
Constitution of diazo-salts.[2]—In order to represent the constitution of diazo-benzene chloride Kekulé in 1866 suggested the formula

$$C_6H_5.N:N.Cl.$$

which offers an easy explanation of the formation of hydrazines by reduction, thus:—

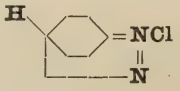
$$C_6H_5.N:NCl + 4H = \underset{H\ \ 3H}{C_6H_5N - NCl}$$

This view was generally accepted until about 1894, when the formula proposed by Blomstrand (1869), Strecker (1871), and Erlenmeyer (1874), viz.:—



was preferred, chiefly owing to the great resemblance which was shown to exist between these salts and ammonium salts as regards their physical and chemical properties. The name "diazonium" dates from this period, it being used to indicate the similarity to ammonium compounds.

The remarkable fact that no amine in which the basic nitrogen atom is attached to a fully saturated ring or complex has furnished a diazo-salt led, in 1907, to the suggestion that diazo-salts may be represented by the formula



and an extension of this involving the idea of a possible oscillation of the linkage

[1] For a comparison of the stabilities of different diazo-salts used technically, see Cain and Nicoll, *J.C.S.*, 1902, lxxxi. 1412; 1903, lxxxiii. 206, 470; also *J. Soc. Dyers*, 1902, April No.

[2] See Morgan, "Our Present Knowledge of Aromatic Diazo-Compounds," *Brit. Ass. Reports*, 1902. Hantzsch, *Die Diazoverbindungen*, 1902. Eibner, *Zur Geschichte der aromatischen Diazoverbindungen*, 1903. Cain, *The Chemistry of the Diazo-compounds*, 1908. Morgan, "Diazo-compounds." Thorpe's *Dictionary of Applied Chemistry*, 1912, vol. ii. page 223.

of nitrogen and the para-carbon atom between this position and the two ortho-positions, thus :—

has the additional advantage of explaining satisfactorily, by means of a simple adaptation, the various diazo-compounds of the non-aromatic series.

CHAPTER V.

HYDROXYL COMPOUNDS (OH). (*Benzene Series.*)

The hydroxyl group may be introduced into the benzene nucleus in a number of ways, of which the following two are the most important :—

(1) By fusing the sulphonic acid, or its alkali salt, with caustic soda,

$$R.\ SO_3Na + 2NaOH \rightarrow R.\ ONa + Na_2SO_3 + H_2O,$$

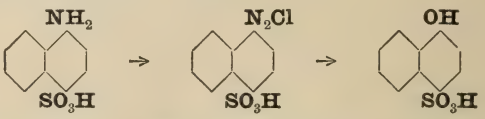
giving rise to the alkali salt of the phenol, sodium sulphite and water.

(2) By boiling the diazo-salt of the amine with water,

$$R.\ N_2Cl + H_2O \rightarrow R.\ OH + N_2 + HCl.$$

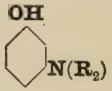
An example of the first method is the production of resorcinol (*m*-dihydroxybenzene) by fusing benzene *m*-disulphonic acid with caustic soda.

The second method is used for the preparation of Nevile and Winther's acid (*α*-naphthol-4-sulphonic acid) from naphthionic acid



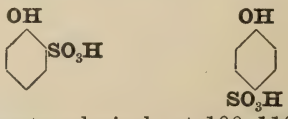
By the nitration of phenol, nitro-phenols are formed, which, on reduction, give the corresponding amidophenols.

The most important of these are the dialkyl *m*-amidophenols



which are largely used in the preparation of the Rhodamines.

Phenol, on treatment with sulphuric acid, is converted into the phenol sulphonic acids, the ortho- and para-derivatives



being formed, the latter almost exclusively at 100–110° C. Its nitroamido- and diamido-derivatives are used for making some important azo-dyestuffs.

Reactions of the hydroxyl group.—Unlike the aliphatic hydroxyl group, the phenol group possesses marked acid properties. Thus with dilute caustic soda it is converted into a sodium salt, stable in aqueous solution. It is not, however, a sufficiently strong acid to decompose carbonates, and it is only by

increasing the negative nature of the phenyl (C_6H_5) group by the entrance of, for example, nitro-groups that the hydrogen of the hydroxyl becomes sufficiently acid for this purpose.

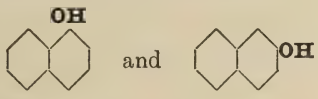
Thus picric acid, $(C_6H_2(NO_2))_3OH$, made by the nitration of phenol, decomposes carbonates.

The hydroxyl group, together with the amido-group, forms a constituent of almost every dyestuff, and it sometimes happens that the acidic nature of this group has a bad effect upon the character of a dyestuff in which it occurs.

This defect is remedied by converting the phenol group (in the finished dye) into its alkyl salt, which can be readily done by treating its sodium salt with alkyl halogen compounds or alkyl sulphates.

HYDROXYL COMPOUNDS (OH). (*Naphthalene Series.*)

The introduction of the hydroxyl group in the naphthalene series is also brought about by fusing the sulphonic acid with caustic soda. Thus the α- and β-naphthalene sulphonic acids give α- and β-naphthol



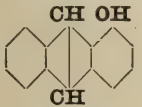
when fused with caustic soda.

Like phenol, both α- and β-naphthol are weak acids, and react with caustic alkalies, forming stable alkali salts.

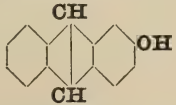
By sulphonation they pass into sulphonic acids, an account of which has already been given.

HYDROXYL COMPOUNDS (OH). (*Anthracene Series.*)

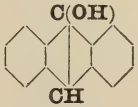
It is evident that there are three monohydroxyl derivatives of anthracene, which may be represented by the formulæ



α-derivative (α-anthrol).



β-derivative (β-anthrol).



Anthranol.

The first two are derived from the corresponding sulphonic acids, and are dealt with on page 119. The third is desmotropic with anthrone $C_6H_4\langle^{CO}_{CH_2}\rangle C_6H_4$, and can be produced by the action of concentrated sulphuric acid on *o*-benzyl-benzoic acid (*Ber.*, 1894, xxvii. 2789) $C_6H_4\langle^{CH_2.C_6H_5}_{CO_2H}$ as well as by other means (*Ann.*, 1911, ccclxxix. 15, 55). Anthrone is insoluble in alkalies, but passes into solution on warming, forming salts of anthranol. Anthranol can be prepared by carefully acidifying this salt with dilute sulphuric acid.

CHAPTER VI.

CARBOXYL COMPOUNDS (COOH).

The carboxylic acids of chief importance in the dyeing industry are those belonging to the benzene series.

The carboxyl group may be introduced in a variety of ways, of which the two following are of importance :—

(1) Oxidation of a benzene hydrocarbon containing a side chain.
Thus toluene on oxidation with manganese dioxide and sulphuric acid yields benzoic acid,

$$C_6H_5CH_3 + 3O \rightarrow C_6H_5COOH + H_2O.$$

(2) The hydrolysis of the nitrile group.
Thus benzonitrile gives benzoic acid (ammonium salt)

$$C_6H_5CN + 2H_2O \rightarrow C_6H_5COONH_4$$

The most important carboxylic acids are :—benzoic acid, salicylic acid, gallic acid, phthalic acid, and tannic acid ; and since no general method can be applied for their production they will be described in detail.

Benzoic acid, C_6H_5COOH, is obtained either by method (1) or from benzotrichloride, $C_6H_5CCl_3$, on heating with water in the presence of an iron salt.

Salicylic acid, $C_6H_4(OH).COOH$ (1 : 2), is prepared by Kolbe's method, that is, by passing carbon dioxide over heated sodium phenate, according to the following equations :—

$$\text{I. } C_6H_5ONa + CO_2 \rightarrow C_6H_5OCOONa.$$

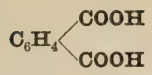
$$\text{II. } C_6H_5.O.COONa \rightarrow C_6H_4\begin{cases}OH\\COONa\end{cases}.$$

$$\text{III. } C_6H_4\begin{cases}OH\\COONa\end{cases} + C_6H_5ONa \rightarrow C_6H_4\begin{cases}ONa\\COONa\end{cases} + C_6H_5OH.$$

A modification of this synthesis, which permits of the immediate conversion of all the phenol into salicylic acid, is known as Schmitt's synthesis. According to this method, the sodium phenyl carbonate is heated in an autoclave under pressure to 140°, when it is completely converted into sodium salicylate according to equation II.

Gallic acid is prepared by boiling gallotannic acid with dilute sulphuric acid. The latter, also known as *tannic acid* or tannin, is obtained from gall-nuts by extracting the powdered nuts with ether and alcohol, and dissolving the tannic acid from the extract by shaking it with water.

Phthalic acid



was formerly produced by oxidising naphthalene or its derivatives with nitric acid or chromic acid. It is now, however, prepared by treating naphthalene with sulphuric acid in the presence of mercury.

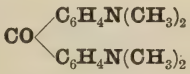
The sulphuric acid plays the part of an oxidising agent, and is itself reduced to sulphurous acid (E.P. 18,221[96]), and the phthalic acid is obtained in the form of its anhydride.

Phthalic anhydride is extensively used in the preparation of the phthaleïns (see p. 100).

KETONES (CO).

Very few of the aromatic ketones find any application in the preparation of dyestuffs.

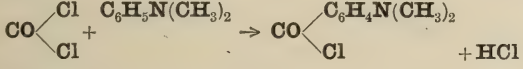
Probably the most important are those derivatives of benzophenone which are used in the production of the compounds of the triphenylmethane series, of which tetramethyldiamidobenzophenone



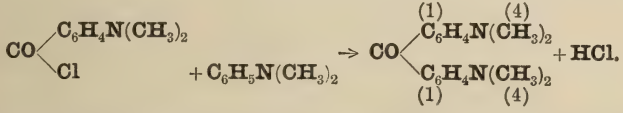
is a type.

This substance is prepared by the action of phosgene ($COCl_2$) on dimethylaniline.

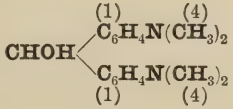
The first product formed in this reaction is evidently dimethylamidobenzoyl chloride



which reacts further with dimethylaniline to form the ketone

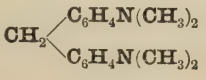


Tetramethyldiamidobenzophenone on reduction yields tetramethyldiamidobenzhydrol



which is also used in the preparation of compounds of the triphenylmethane series.

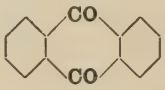
This secondary alcohol may be also (and better) prepared by the oxidation of tetramethyldiamidodiphenylmethane



which is formed by the condensation of formaldehyde and dimethylaniline

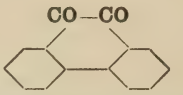
$$CH_2O + \begin{matrix} C_6H_5N(CH_3)_2 \\ C_6H_5N(CH_3)_2 \end{matrix} \rightarrow CH_2 \begin{matrix} C_6H_4N(CH_3)_2 \ (1)\ (4) \\ C_6H_4N(CH_3)_2 \ (1)\ (4) \end{matrix} + H_2O$$

An important ketone, belonging to the anthracene series, is *anthraquinone*



which is prepared by oxidising anthracene with chromic acid. The monosulphonic acid, when fused with caustic soda, gives alizarine, and the two disulphonic acids, which are obtained on further sulphonation, furnish isopurpurine and flavopurpurine respectively.

Phenanthraquinone



is similarly prepared from phenanthrene by oxidation with chromic acid.

ALDEHYDES (CHO).

The most important aromatic aldehyde used in the manufacture of the dyestuffs is *benzaldehyde*.

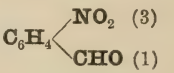
It is prepared by heating benzyl chloride with manganese dioxide and water (1), or by heating benzyl chloride containing benzotrichloride, $C_6H_5CCl_3$, with milk of lime (2)

(1) $C_6H_5CH_2Cl + O \rightarrow C_6H_5CHO + HCl$

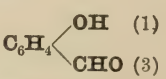
(2) $C_6H_5CHCl_2 + Ca(OH)_2 \rightarrow C_6H_5CHO + CaCl_2 + H_2O$

and is used for the preparation of Malachite green. The nitro-derivatives of benzaldehyde are of considerable importance.

m-Nitrobenzaldehyde

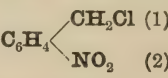


is the only one easily prepared by direct nitration, and gives, on reduction, *m*-amidobenzaldehyde, which, on diazotisation and boiling with water, is converted into *m-hydroxybenzaldehyde*

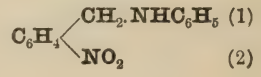


used in the preparation of dyestuffs of the patent blue type (see page 82).

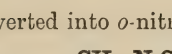
o-Nitrobenzaldehyde is utilised in the preparation of artificial Indigo (M.L.Br.). It is prepared (*Homolka*) by condensing *o*-nitrobenzyl chloride



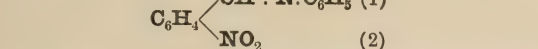
with aniline to form the benzyl derivative



which, on oxidisation, is converted into *o*-nitrobenzylidene aniline



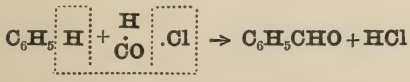
giving, on hydrolysis with acids, *o*-nitrobenzaldehyde and aniline



The Gattermann processes for the preparation of aldehydes are of exceptional interest.

One of these consists in passing dry carbon monoxide and hydrochloric acid gas (at 60–70° C.) through a mixture of cuprous chloride and aluminium chloride with the aromatic hydrocarbon into which it is desired to introduce the aldehyde group.

The mixture of carbon monoxide and hydrogen chloride apparently reacts as the non-existent formyl chloride, which, like other acid chlorides, reacts on the hydrocarbon according to the equation



Another process consists in treating phenols with hydrocyanic acid and hydrochloric acid in the presence of aluminium chloride.

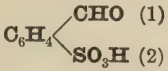
The products first formed are aldimides (containing the group – CH : NH), which are dissociated by the action of hydrolytic agents into the aldehyde and ammonia.

This method gives better results in the naphthalene series than in the benzene series, and has been used by its inventor in the preparation of a number of important aldehyde derivatives of naphthalene.

It has also been found (B.A.S.F.) that the aldehyde group can be introduced by the oxidation of the methyl group (CH_3) contained in aromatic hydrocarbons.

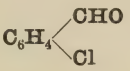
Thus toluene can be converted into benzaldehyde by oxidation with manganese dioxide and sulphuric acid.

The ortho-sulphonic acid of benzaldehyde



is used in the manufacture of dyestuffs of the patent blue class.

It is prepared by heating *o*-chlorobenzaldehyde



with sodium sulphite.

Formaldehyde, H.CHO, owing to the many reactions into which it enters, is the most important aliphatic compound used as an intermediate product. It is also used under the name of formalin (40 per cent. solution) as a disinfectant.

The method of preparation consists in oxidising the vapours of methyl alcohol by atmospheric oxygen, in the presence of an oxygen carrier.

Phosgene, $COCl_2$, is prepared by passing carbon monoxide and chlorine over cooled animal charcoal, and by the action of fuming sulphuric acid on carbon tetrachloride. It is used in the preparation of the ketones described on p. 31, which are employed in the manufacture of dyestuffs of the triphenylmethane series.

§ 2.—*THE DYESTUFFS.*

CHAPTER VII.

APPLICATION OF THE DYESTUFFS.

Many theories have, from time to time, been brought forward having for their object the elucidation of the nature of dyeing.

Among these may be mentioned :—

(I.) The mechanical theory.
(II.) The chemical theory.
(III.) The solid solution theory.
(IV.) The absorption theory.

None of these, however, satisfactorily explains the facts, and the nature of dyeing must be regarded as still but little understood.

The *mechanical theory* supposes a purely mechanical absorption of the dyestuff by the "pores" of the fibres, which, on being closed by astringents, retain the colour.

The *chemical theory* supposes a direct combination between the dye-base and the fibre, which is (in the case of wool) presumed to possess both acid and basic properties.

One of the chief facts in support of this theory was that discovered by Knecht, who found that, when Magenta (hydrochloride) was boiled in aqueous solution with wool, the whole of the hydrochloric acid remained in the bath, whilst the dye-base (colourless) combined with some acid constituent of the wool to form the colour.

Since then, however, it has been shown that the rosaniline base in one of its forms is coloured, and that the dissociation of the rosaniline hydrochloride is completely brought about by boiling its aqueous solution with such inert substances as glass, etc.

As a matter of fact, the laws of chemical combination are not followed in dyeing, and the theory cannot be regarded as adequately expressing the facts.

The *solid solution theory* supposes that the fibre plays toward the dyestuff the part of a solid solvent. Here, again, however, the laws of solution are not generally obeyed, and the theory must be regarded as inadequate.

The *absorption theory*, recently proposed by v. Georgievics, states that "dyeing is a phenomenon of absorption, the dye being retained on, and in, the fibre by adhesion."

For an account of this theory the reader is referred to Prof. v. Georgievics' *Chemical Technology of the Textile Fibres*, translated by Ch. Salter, p. 130.

The classification of the dyestuffs from the practical standpoint, as mentioned in the previous chapter, is best considered from the point of view of their behaviour towards the various fibres.

CLASSIFICATION OF THE DYESTUFFS (*Schaposchnikoff*).

CLASS I. Colours with Acid Character.		CLASS II. Colours having the Character of Salts.	CLASS III. Colours with Basic Character.	CLASS IV. Colours with Indifferent Character.	
Group I. Dyestuffs that dye in an acid bath.	**Group II.** Dyestuffs that dye on metallic mordants.	**Group III.** Dyestuffs that dye in neutral or alkaline baths.	**Group IV.** Dyestuffs that dye in a neutral bath.	**Group V.** Dyestuffs developed on the fibre.	**Group VI.** Dyestuffs caused to adhere mechanically to the fibre.
(1) Nitro-dyestuffs.	(6) Certain azo-dyestuffs (Alizarine yellow, Diamond yellow, Azarine, etc.).	(12) Dyestuffs from tetrazo-salts (derivatives of benzidine, etc.).	(15) Basic azo-dyestuffs (Chrysoidine, etc.).	(19) Metals.	(25) Albumen colours (dyestuff fixed on the fibre by means of albumen, casein, etc.).
(2) Most azo-dyestuffs (amidoazo-, azoxy-, and disazo-dyestuffs).	(7) Oxyquinone and quinoneoxime dyestuffs.	(13) Thiazole dyestuffs (Primuline, etc.).	(16) Di- and triphenylmethane dyestuffs.	(20) Insoluble azo-compounds.	
(3) Sulphonic acids of the triphenylmethane, Induline, and Quinoline dyestuffs — Indigo-carmine.	(8) Some quinoneimide dyestuffs (Gallocyanine).	(14) Certain natural colouring matters, sulphine dyestuffs.	(17) Most of the quinoneimide dyestuffs (Indamines, Thiazines, Oxazines, Azines, etc.).	(21) Mineral colours.	
(4) Hydrazone and pyrazolone dyestuffs.	(9) Oxyketone, xanthone, and flavone dyestuffs.		(18) Quinoline and acridine dyestuffs.	(22) Indigo and Indophenol.	
(5) Chromotropes (also belong to the next group).	(10) Phthaleïne and rosolic acid dyestuffs.			(23) Aniline black.	
	(11) Natural dyestuffs.			(24) Certain natural colours (catechu, etc.).	

Note.—The Indanthrene colours would be included in Class 22.

They may in this way be divided into six classes :—

(1) Acid dyestuffs.
(2) Basic or tannin dyestuffs.
(3) Dye-salts or substantive cotton dyes.
(4) Mordant dyes.
(5) Vat dyes.
(6) Developed dyes.

The term *substantive* dyes means that the dye possesses direct affinity for the particular fibre to which it is substantive.

The term *adjective* means that it has no direct affinity for the particular fibre, but that it can be affixed to it by the acid of some third substance, *i e.* a mordant.

(1) **Acid dyestuffs** are the sodium salts of the sulphonic acids, as well as of such dyes as certain phenol groups associated with nitro-groups.

They are substantive to wool, upon which they affix themselves from a bath acidified with potassium hydrogen sulphate or dilute sulphuric acid.

They do not form lakes with tannin, and hence can readily be distinguished from the basic or tannin dyes. They have little affinity for cotton, and are rarely used for dyeing this fibre.

(2) **Basic** or **tannin dyestuffs.**—These are mostly colour bases with hydrochloric acid or zinc chloride. Although they are substantive to wool and can be readily affixed to this fibre, yet they are, at the present day, almost exclusively used for the printing of cotton on a tannin mordant.

Wool takes up the basic dyes in a very uniform manner without the aid of any addition to the dye-bath.

Cotton.—The basic dyestuffs are to a certain extent substantive to cotton, but the colours obtained are extremely fugitive, and of little practical importance.

The best method of dyeing cotton with these colouring matters is first to prepare the material with either

(*a*) Tannic acid and tartar emetic.
(*b*) A fatty acid salt of alumina.

In either case the colour is produced by heating the mordanted cotton in a bath of the dyestuff at 60° C. for half to one hour.

The use of a fatty acid salt of alumina instead of tannic acid and tartar emetic in some cases produces a very marked difference in the colour of the dyed material.

Thus the Rhodamines, when dyed on a fibre mordanted with tannin, produce a dull lilac shade ; whereas the corresponding dyeings on a cotton impregnated with a fatty acid are of an extremely brilliant shade of pink, closely resembling the colour produced by the action of the Rhodamines on wool.

The fatty acid used for this purpose is known as Turkey-red oil, a description of which will be given under the head of the mordant colours.

(3) **Direct** or **substantive cotton dyes** (salt colours).—The discovery of the direct cotton dyes in 1884 by Böttiger caused a revolution in the cotton-dyeing industry. They are for the most part azo-compounds derived from benzidine

$$\begin{matrix} C_6H_4NH_2 \\ | \\ C_6H_4NH_2 \end{matrix}$$

or from bases which are similar to benzidine in their constitution.

A further description of them will be given under the head of the azo-dyes, and it is only necessary to mention here that the relation between the property of a dyestuff of affixing itself directly on the cotton fibre and its constitution is not yet clearly defined.

The substantive cotton dyes are surpassed in brilliance by the basic dyes and in fastness by the mordant colours; moreover, they are more susceptible than these to impurities in the material and to injury during the finishing processes.

Many of the substantive cotton dyes are better adapted for the dyeing of wool than of cotton. The method of their application is the same as that of the acid dyestuffs.

(4) **Ingrain colours.**—It frequently happens that the substantive dyestuff employed for the dyeing of the cotton fibre contains a free amido-group, which is, in many instances, capable of further diazotisation. When this is the case, the absorbed dye may be treated directly on the fibre with nitrous acid, which, converting the amido-group into the diazo-group, causes it to combine with any naphthol or amine capable of serving as a second component. In this way fast shades of colour can be produced.

(5) **The mordant dyes** consist of a large number of very differently constituted dyes, all of which possess an acid character, and are indebted to the presence in their molecule of hydroxyl or carboxyl groups for their property of forming lakes with mordants.

The methods by which the mordant colours can be affixed to the fibres are very diverse, depending (1) upon the nature of the dyestuff and (2) upon the fibre. It is proposed here to deal merely with a few typical examples.

Wool.—It is in the dyeing of wool that the mordant dyestuffs receive their most important application. Roughly speaking the methods are of two kinds:—

(*a*) Dyeing previously mordanted wool.
(*b*) Dyeing in a single bath.

Cotton.—The most important application of the mordant dye to cotton is in the dyeing of Turkey-red.

This colour, which has been known from the earliest times, is produced on the cotton fibre by the interaction of alizarine, alumina, lime, and fatty acid.

The exact chemical nature of the process is not yet definitely understood, although it has been found (*Rosenstiehl*) that the formation of the lake from alizarine and alumina cannot take place except in the presence of lime, a fact which was confirmed by Liechti and Suida, who found that all Turkey-red dyeings contain lime.

The part played by the Turkey-red oil is still obscure.

(6) **Vat dyes.**—To this class belong Indigo, Indophenol, and to a certain extent the sulphur colours.

The dyestuffs are insoluble in water, and therefore cannot be used directly for dyeing. However, on reduction, they are converted into "leuco"-compounds,[1] which are soluble in dilute alkali, have (in this condition) a marked affinity for the fibre, and further possess the property of being readily reconverted into the dyestuff by the action of weak oxidising agents

Consequently, in order to dye with these compounds it is only necessary to impregnate the fibre with the reduced dye in alkaline solution, and by exposing it to the action of the air to cause the reoxidation of the leuco-compound

[1] The "leuco"-compounds from the Indanthrene series are coloured substances.

to the insoluble dyestuff, which then remains firmly fixed in and on the fibre. The colours produced in this manner are among the fastest known, and research during the last few years has revealed the existence of a large number of substances belonging to this group, which, under the names of the Indanthrene colours, the Algol colours, the Ciba colours, etc., have enabled the dyer to produce almost any shade of colour by this process. A description of these compounds is given later.

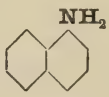
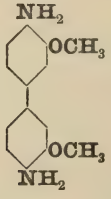
(7) **The developed dyes**, as their name implies, are developed on the fibre by the interaction of the constituents which produce them.

They may be divided into two classes :—

(*a*) The ice-colours.
(*b*) Aniline black.

(*a*) The *ice-colours* are produced on the cotton fibre by the interaction of some second component (with which the fibre has been impregnated) with a solution of a diazo-salt cooled with ice.

The nature of the amine varies the colour considerably, as is shown by the following list:—

		With β-naphthol.
p-nitraniline		Scarlet.
α-naphthylamine . . .		Bordeaux (claret).
Benzidine		Brown.
Dianisidine		Blue.

(*b*) *Aniline black* is the black formed by the oxidation of an aniline salt, and may be produced either by oxidising a fibre impregnated with an aniline salt, or by heating the fibre with a solution of an aniline salt containing an oxidising agent.

The *first* and older *method* is performed by padding the fibre with a solution of aniline hydrochloride containing the oxidising agent (potassium chlorate) with ammonium chloride and a salt of vanadium (oxygen carrier), the black being developed by the process known as ageing, which consists in subjecting the impregnated fibre to the action of air at a moderately high temperature.

The *second method* consists in dyeing the fibre in a bath containing aniline hydrochloride, potassium bichromate, and either hydrochloric or sulphuric acid.

CHAPTER VIII.

CLASSIFICATION OF THE DYESTUFFS.

The large number of organic dyestuffs which have been synthetically prepared show that the dyeing property is dependent upon structure, and that the dyestuffs belong to certain well-defined classes of organic compounds.

This has been expressed by O. N. Witt in the following way :—

(I.) The character of a dyestuff is derived from some group contained in it, which he calls the "chromophore."

(II.) The fundamental substance containing the chromophore he calls the "chromogen."

(III.) The "chromogen" is not a dyestuff, but is converted into this by the entrance of some salt-forming group which destroys the chemically inert character of the chromogen.

The best example illustrating this generalisation by Witt is amidoazobenzene, $C_6H_5N : N.C_6H_4NH_2$. Here the chromophore group is the azo-group, $-N=N-$; the chromogen is azobenzene, $C_6H_5N : N.C_6H_5$, which is not a dyestuff, but becomes the base of one by the introduction of the amido-group, which confers salt-forming properties upon it.

The groups which confer salt-forming properties upon the chromogen are usually the amido-group (NH_2) and the hydroxyl group (OH), and these are termed by Witt the "auxochromes."

Speaking generally, only those organic compounds which contain either acid or basic groups can be dyestuffs.

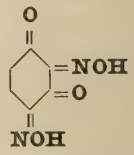
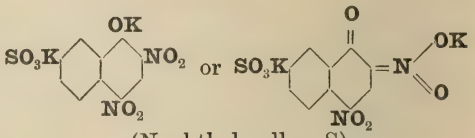
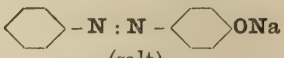
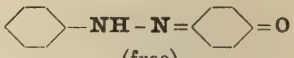
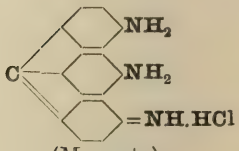
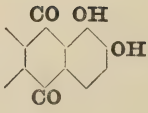
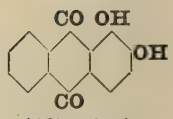
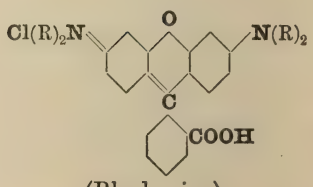
Furthermore, they are "unsaturated" compounds, and are readily reduced by nascent hydrogen, passing either into "leuco"-compounds, which yield the dyestuff again on oxidation, or breaking up into bodies of lower molecular weight, which are not reconverted into the dyestuff by oxidation.

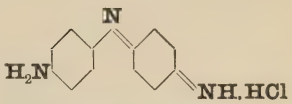
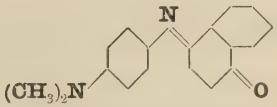
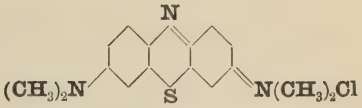
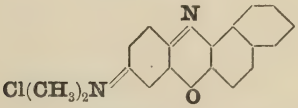
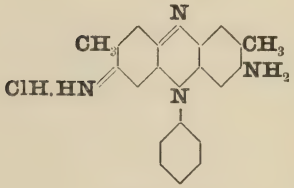
This important behaviour of the dyestuffs will be again referred to, since it is used as a means of identifying them, both on the fibre and in their solid state.

The theoretical classification of the dyestuffs is based upon the generalisation by Witt above referred to, that is to say, according to the chromophore group occurring in them.

For practical purposes, however, it is far more convenient to classify them according to their behaviour on dyeing the textile fibres, and this method will be adopted in dealing with their experimental application in a later chapter.

The classification, according to structure, divides them into the following chief groups :—

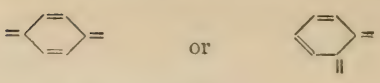
Name of Dyestuff Group.	Chromophore.	Typical Dyestuff.
(1) Nitroso or oxime . .		 (Resorcin green).
(2) Nitro . . .		 (Naphthol yellow S)
(3) Azo . . . . (*a*)	$-N=N-$	 (salt).
(*b*)		 (free) (*p*-oxyazobenzene).
(4) Triphenylmethane .		 (Magenta).
(5) Oxyketone (mordant) .		 (Alizarine).
(6) Pyronines . .		 (Rhodamine).

Name of Dyestuff Group.	Chromophore.	Typical Dyestuff.
(7) Diphenylamine . .	=⟨⟩=	
(*a*) Indamines . .		 (Phenylene blue).
(*b*) Indophenols .		 (Indophenol blue).
(*c*) Thiazines .		 (Methylene blue).
(*d*) Oxazines . .		 (Meldola's blue).
(*e*) Safranines . .		 (Safranine).

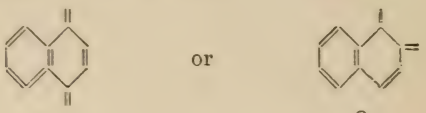
The relationship between colour, that is, the production of absorption bands in the visible range of the spectrum, and the presence of conjugated linkages within the molecule has, within recent years, been clearly established.

Although philosophically incorrect, it is necessary from the point of view of colour chemistry to distinguish between visible and invisible colour. Thus the researches of Hartley, Baly, and others have shown that the many apparently colourless substances which contain the various aromatic nuclei, such as, for example, the hydrocarbon benzene, produce definite absorption bands in the ultra-violet region of the spectrum. Consequently, these colourless substances may reasonably be regarded as possessing colour which cannot be detected by the eye.

It has been shown that it is possible so far to retard the intra-molecular vibrations within the aromatic nuclei which produce ultra-violet absorption so as to throw the absorption into the visible range of the spectrum, and hence lead to visible colour. This effect is always produced when the "quinone linkage" appears in an aromatic compound, and, consequently, every substance which contains this linkage is visibly coloured. The quinone linkage may be either benzenoid, such as the para- or ortho- forms :—

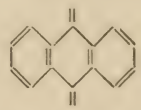


or in the naphthalene series may be either



α β

The same linkage appears in anthraquinone



and is present in members still higher in the series, such as indanthrene (*q.v.*).

In fact, it is probable that the *cause* of visible colour in all organic dyestuffs of the aromatic series can be ascribed to the presence in them of one or more quinone linkages, and since the only dyestuffs of importance belong to the aromatic series, it may be stated that that form of conjugated double linkages which is known as the quinone linkage is the sole chromophore in the Witt sense of the term.[1]

Mordant dyestuffs.—The term *mordant* is applied to some substance which will form coloured *lakes* with dyestuffs.

Thus the basic dyestuff Magenta, which is readily absorbed by wool, has little or no affinity for the vegetable fibres, but possesses the property of forming with tannic acid an insoluble coloured lake. Hence by steeping the cotton fibre in a solution of tannic acid, and subsequently fixing it in the fibre by means of tartar emetic (which forms an insoluble compound with tannic acid), a vegetable fibre impregnated with a salt of tannic acid can be obtained, which, on boiling in a solution of Magenta hydrochloride, becomes coloured with the tannic lake of Magenta. Hence tannic acid is, strictly speaking, a mordant. The term, however, has a somewhat more restricted meaning, and is applied to certain metallic oxides which possess the property of forming coloured lakes with certain well-defined classes of organic compounds.

It has been found (*Liebermann* and *v. Kostanecki*) that only those derivatives of anthraquinone which contain the hydroxyl groups in the ortho-position to themselves, and to one of the carboxyl groups of the chromophore, possess the property of forming lakes with the oxides of various metals, such as iron, tin, aluminium, chromium, etc.

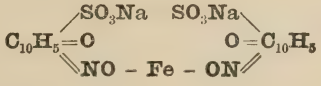
The formation of these lakes can be brought about by steeping the cotton fibre in a solution of the acetate of the metal, which, on steaming, becomes impregnated with the oxide (owing to the decomposition of the acetate). The cotton thus mordanted, when boiled in an aqueous solution of the dyestuff, becomes dyed with the lake.

The law of Liebermann and v. Kostanecki is not of general application, and many instances are known which do not conform to it.

There are, however, many ortho-derivatives, outside the alizarine series, which form lakes with mordants. Thus azo-compounds such as $C_5H_5N:N.C_6H_3(OH)COOH$ prepared from salicylic acid and diazobenzene chloride, form lakes with metallic oxides, and thus compounds of this type, which are already dyestuffs, can be converted into lakes by treatment on the fibre with metallic mordants.

[1] It is still open to question whether the azo-colouring matters fall within this generalisation.

This property is also possessed by certain of the nitroso-phenols ; thus naphthol green B (Cassella) is the iron compound of sodium nitroso-β-naphthol mono-sulphonate



(See p. 44.)

CHAPTER IX.

THE NITROSO-COMPOUNDS. (*Quinoneoximes.*)

The nitroso-phenols are produced by the action of nitrous acid on the phenols, according to the equation

The fact, however, that the same nitroso-phenol is produced by the action of hydroxylamine on *p*-quinone according to the equation

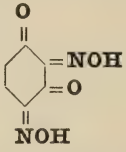
quinone — quinoneoxime

shows that in all probability these substances can react as quinoneoximes, which better accounts for their behaviour as dyeing agents, since the quinone ring

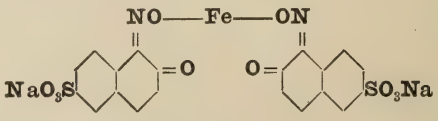
occurs in many dyestuffs as a chromophore.

The value of the nitroso-dye more especially depends upon the property of the ortho-compounds of forming lakes (green) with iron.

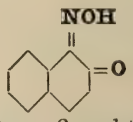
Thus *Fast green* or *Resorcin green* is dinitrosoresorcinol, which is produced by the action of nitrous acid on resorcinol, and therefore possesses the formula



Naphthol green B [C] is the iron-compound of sodium nitroso-β-naphthol mono-sulphonate, and has the formula

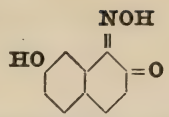


Other dyestuffs of this group are :—

Gambine Y [H] . . . 

α-nitroso-β-naphthol.

Dioxin [L]
Gambine B [H] } . . .



nitrosodihydroxynaphthalene.

These dyestuffs are only sparingly soluble in cold water, and are found in commerce either in the solid form or suspended in water (paste).

CHAPTER X.

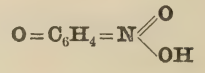
THE NITRO-COMPOUNDS.

The entrance of the nitro-group into the molecule of the aromatic phenols causes them to become more or less pronounced dyestuffs.

The nitro-dyestuffs are, without exception, acid-dyestuffs; that is to say, they are the salts of the various nitro-phenols and nitro-naphthols (or their sulphonic acids) formed by the action of alkalies on the strongly acid hydroxyl compounds containing nitro-groups in the same nucleus.

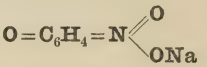
Many of the nitro-phenols, as, for example, *p*-nitrophenol, are colourless, but in the form of their salts are coloured. *o*-Nitrophenol, on the other hand, is itself a coloured substance.

It has been suggested (*Armstrong*) that this difference between the ortho- and para-derivatives might possibly be due to a difference in structure. Thus for para-nitrophenol (colourless) he proposes the ordinary nitro-formula, $OH.C_6H_4.NO_2$; but for the yellow ortho-compound he considers the quinone structure

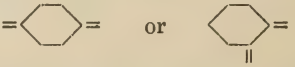


the more probable one.

The formation of coloured salts from *p*-nitrophenol would, however, seem to indicate that this substance in the form of the free acid has the ordinary nitro-structure; but that in the form of its salts it possesses a quinone structure represented by the formula



The close analogy that exists between the nitro-compounds and the so-called nitroso-dyestuffs renders it probable that a similar structure is possessed by both, and that the nitro-dyestuffs are derivatives of quinone, having for their chromophore the quinone ring

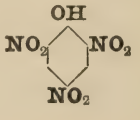


The nitro-compounds belong to the older artificial dyestuffs, and were at one time very largely used by the dyer for the purpose of dyeing wool and silk. Their fugitive character has, however, led in recent times to their replacement by the yellow azo-dyes.

Most of them possess the properties characteristic of aromatic nitro-compounds; that is to say, their more or less pronounced yellow colour, the explosive nature of their salts, and their poisonous character.

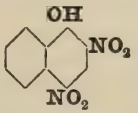
Typical examples of the nitro-dyestuffs are:—

Picric acid,



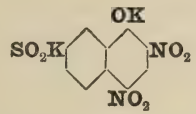
which is the oldest dyestuff of the group, and is prepared by treating phenol sulphonic acid with dilute nitric acid. Although at one time of considerable importance, it is at the present time but little used in dyeing, but is very largely employed in the manufacture of explosives, such as melinite, lyddite, and shimose.

Martius yellow, the sodium, calcium, or ammonium salt of dinitro-α-naphthol



is prepared by the nitration of 1-naphthol-2 : 4-disulphonic acid, and was at one time largely used for the dyeing of wool. At the present time it is employed as a pigment colour and for colouring soap.

Naphthol yellow S is the potassium (or sodium) salt of 2 : 4-dinitro-1-naphthol-7-sulphonic acid



and is the most important dyestuff of the group.[1]

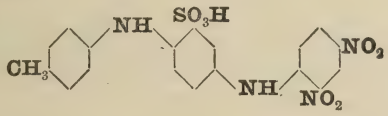
It is prepared either

(1) By the nitration of 1-naphthol-2 : 4 : 7-trisulphonic acid, or

(2) By the nitration of nitroso-α-naphthol-2 : 7-disulphonic acid (usual method).

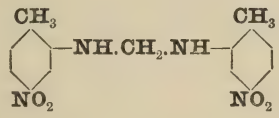
Naphthol yellow is much faster than the other nitro-dyestuffs, and is extensively used for dyeing the animal textile fibres.

Amido yellow E [M],



is prepared by condensing amidotolylphenylaminesulphonic acid with chlorodinitrobenzene (E.P. 13,672 of 1912, A.P. 1,059,571, F.P. 443,809, D.P. 263,655).

Pigment chlorin G G



obtained by condensing nitrotoluidine with formaldehyde, and *Lithol fast yellow* G G [B] similarly prepared from 3-chloro-6-nitraniline are employed for making lakes.

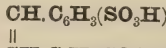
THE STILBENE DYESTUFFS.

The dyestuffs of this group are prepared by heating *p*-nitrotoluenesulphonic acid or dinitrodibenzyldisulphonic acid with caustic soda under various conditions of temperature, concentration, etc., either alone or together with amines, oxidising agents, etc.

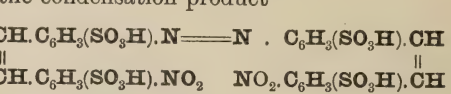
[1] See Knecht and Hibbert, *Ber.*, 1904, xxxvii. 3475.

They were formerly considered to be nitroso- or azoxy-stilbene derivatives, but Green and his pupils[1] have proved that they must be regarded as azo-dyestuffs. The action of caustic soda on *p*-nitrotoluenesulphonic acid gives rise to a dinitroso-stilbenedisulphonic acid. Two molecules of this now condense, one molecule being oxidised by the other, and the two nitrogen atoms, which are deprived of their oxygen atoms, combine to form the azo-group.

The first compound formed has the formula

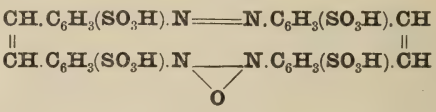


and this then gives the condensation product



This is the composition of *Stilbene yellow* 8 G [Cl. Co.], which is the greenest yellow of the series.

Direct yellow RT [Cl. Co.], *Direct yellow* F [Sch.], or *Naphthamine yellow* G [K], is considered to have the constitution



When the interaction of *p*-nitrotoluensulphonic acid and caustic soda is allowed to take place in the presence of oxidisable substances, such as glycerol, starch, etc., the product contains two stilbene molecules linked together by two azo-groups. The dyestuff is known as *Stilbene orange* 4 R [Cl. Co.] or *Chloramine orange* G [By].

Diphenylcitronine G [G] is prepared by condensing dinitrodibenzyldisulphonic acid or dinitrostilbenedisulphonic acid with caustic soda and aniline, and *Curcuphenine* [Cl. Co.] by condensing *p*-nitrotoluenesulphonic acid with dehydrothio-*p*-toluidinesulphonic acid in weak alkaline solution.

Diphenyl fast yellow [G] is the product of condensation of dinitrodibenzyldisulphonic acid or dinitrostilbenedisulphonic acid with dehydrothio-*p*-toluidinesulphonic acid or primulinesulphonic acid through the agency of caustic soda.

[1] *J.C.S.*, 1904, lxxxv. 1422, 1432; 1906, lxxxix. 1602; 1907, xci. 2076; 1908, xciii. 1721; *J. Soc. Dyers*, 1907, xxiii. 162.

CHAPTER XI.

THE AZO-DYESTUFFS.

The azo-dyestuffs form a well-defined group of compounds which may, for convenience, be regarded as possessing the chromophore group $-N=N-$.

This divalent group attached to two aromatic nuclei forms the chromogen $R.-N=N-R.$, which, by the entrance of the auxochrome (NH_2 or OH), becomes the base or acid of which the dyestuff is the salt.

On the other hand, it must be remembered that the azo-compounds in their hydrazone forms have the quinone rings $=\bigcirc=$ and $=\underset{\|}{\bigcirc}$ as chromophores, and that the chromogen is, therefore, $R.-NH-N=\bigcirc=$ or $R.-NH-N=\underset{\|}{\bigcirc}$; this question is discussed later in the present chapter.

I. General methods of formation.—Generally speaking, the azo-compounds are prepared by the interaction of a diazo-salt (first component) with an aromatic hydroxy-compound or amine (second component), the reaction proceeding according to the equation

$$R.\,N_2Cl + R.\begin{matrix}OH\text{ or}\\NH_2\end{matrix} \rightarrow R.\,N_2\,R.\begin{matrix}OH\text{ or}\\NH_2\end{matrix} + HCl.$$

(Oxyazo- or amidoazo-compound.)

The two chief methods of formation are as follows:—

(1) The second component is a phenol (naphthol).

The aqueous solution of the salt (hydrochloride) of a primary amine is first treated with sodium nitrite and hydrochloric acid in the presence of ice, whereby a diazo-salt is formed,

$$C_6H_5NH_2HCl + NaNO_2 + HCl \rightarrow C_6H_5N_2Cl + NaCl + 2H_2O.$$

The solution of the diazo-salt is next "coupled" with the phenol by allowing the solution of the former to run gradually into an alkaline solution of the latter.

It is necessary to keep the solution alkaline throughout the addition, since the formation of the azo-compound is retarded by the presence of free mineral acid.

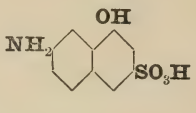
When the dissolved diazo-compound has been mixed with the phenol, the whole is left for the reaction to attain completion, a point which is ascertained by testing a portion of the mixture for unchanged phenol by means of a solution of diazobenzene chloride.

The dyestuff in some cases settles down as a sparingly soluble alkali compound; in others it remains in solution, and can be recovered as a salt by precipitation with sodium chloride, or in the free state by the addition of acid.

(2) The second component is an amine.

The principle of the method is the same, except that the combination of the diazo-salt with the dissolved amine is brought about in neutral or faintly acid solution.

When the second component contains both a hydroxyl and an amido-group, the constitution of the azo-compound obtained varies according as the coupling takes place in acid or alkaline solution. Thus in the case of amido-naphthol sulphonic acid γ



if diazotised benzidine be the first component, one obtains—

In acid solution . . .	Diamine violet.
In alkaline solution . . .	Diamine black.

(See, however, p. 53.)

In the case of dihydroxy-compounds the coupling is often carried on in weak acid solution in order to avoid the formation of a disazo-compound (coupling with reference to both OH groups).

The formation of the azo-compound is usually quantitative, and in the preparation the calculated quantity of the constituents is used.

The best method for preparing the solution of the diazo-salt is to take 1 mol. of the amine, 1 mol. of sodium nitrite, and $2\frac{1}{2}$ mols. of hydrochloric acid, the $\frac{1}{2}$ mol. in excess being subsequently destroyed by the addition of the requisite quantity of sodium acetate, the free acetic acid thus formed having no deterrent effect upon the formation of the azo-dye.

The stability of the diazo-salts varies considerably. In some cases they readily decompose into nitrogen and the corresponding phenols at temperatures above 10° C., and in these cases the diazotisation has to be effected in the presence of ice.

Hence when working with aniline, toluidine, and other bases of this type ice must be used in their diazotisation.

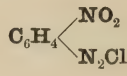
The diazo-sulphonic acids, such as diazo-sulphanilic acid and diazonaphthionic acid, are more stable, and can in many cases be prepared at ordinary temperatures (cp. *J.C.S.*, 1902, lxxxi. 1412; 1903, lxxxiii. 206, 470).

The diazo-compound of *o*-dianisidine is remarkably stable, and can be heated for a long time at 100° C. without undergoing complete decomposition (cp. *J.C.S.*, 1903, lxxxviii. 688).

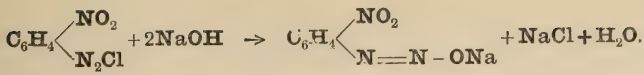
Stable diazo-compounds which can be stored in the solid state, and which can be easily used by the dyer, find considerable application, since they are used in the preparation of the "developed" or "ice" colours.

Many methods have been devised for their preparation.

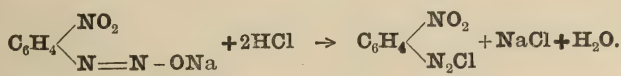
(1) The Badische Anilin und Soda Fabrik treat the diazo-chloride of para-nitraniline



with alkali, which converts it into a stable so-called nitrosamine salt (anti-salt), according to the equation



This sodium salt they introduce under the name *nitrosamine red in paste.* It is quite stable under ordinary conditions, and is quantitatively converted into the diazo-chloride on treatment with dilute hydrochloric acid



(2) Various other firms obtain stable diazo-compounds by evaporating their strongly acid solutions at 45° C. in a vacuum, and mixing them with anhydrous sodium sulphate. Azophor red PN, Nitrazol C, Azogen red, and Benzonitrol are diazo-*p*-nitraniline; Azophor blue D is diazo-*o*-dianisidine.[1]

II. Laws regulating the formation of azo-compounds.—In coupling diazo-salts with phenols and amines of the benzene series, it appears to be a law that the diazo-group enters the para-position with regard to any hydroxyl or amido-group present.

Should this position be occupied, the diazo-group enters the ortho-position to the OH or NH_2; and if this also is occupied, then either, as is most frequently the case, no formation of azo-compound takes place, or the group occupying the para-position is displaced by the diazo-group.

When phenols containing free ortho- and para-positions are coupled with diazo-salts in caustic alkali solution, a small quantity of an orthoazo-compound is formed in addition to the paraazo-compound.

Diamido- and dioxy-derivatives of benzene also combine with diazo-salts to form azo-compounds; but it has been found that this formation only takes place when the diamido- and dioxy-derivatives belong to the meta-series. Thus only *m*-phenylenediamine and resorcinol react with diazobenzene chloride to form azo-compounds.

The dyestuff produced from the former is named "Chrysoidine," and hence this generalisation is known as the "Chrysoidine law."

This "law," however, only applies to the coupling of the diazo-salt under ordinary conditions, since it has been found (*Witt* and *Johnson*) that both pyrocatechol and hydroquinone can furnish azo-compounds with diazobenzene chloride under suitable conditions. Speaking generally, the formation of ortho-oxy- and orthoamido-azo-compounds is desirable when the product is required for use as a dyestuff, since the paraazo-compounds are not so well adapted for this purpose.

If, however, it is desired to prepare polyazo-compounds by the further diazotisation of an amidoazo-compound, then the combination must be effected in the para-position, since amido-groups in the ortho-position to the azo-group are for the most part incapable of reacting with nitrous acid to form diazo-salts.

The laws regulating the formation of azo-compounds in the naphthalene series are as follows:—

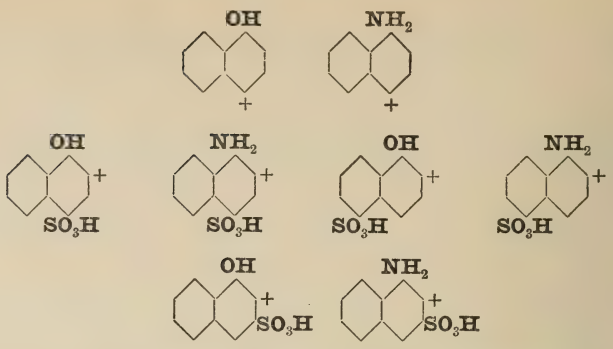
(I.) A hydroxyl group or an amido-group is in the α-position (1).

Combination takes place in the position (4).

If this is occupied, or if the positions (3) or (5) are occupied by sulphonic acid groups, combination takes place in the position (2).

The cross indicates the position of the entering azo-group in the following compounds:—

[1] Paranil is a stable compound of diazo-*p*-nitraniline and naphthalene-β-sulphonic acid, $NO_2.C_6H_4N_2.SO_3.C_{10}H_7 + NaSO_3.C_{10}H_7 + H_2O$.



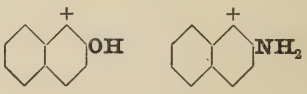
The presence of the sulphonic acid group in any position other than (3), (4), and (5) causes the combination to take place in (4).

This also applies to the disulphonic acid derived from α- and β-naphthol and naphthylamine.

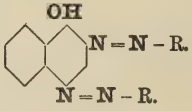
(II.) A hydroxyl group or amido-group is in the β-position (2).

Combination takes place in the position (1); if this position is occupied, then no formation of azo-compound takes place.

Thus β-naphthol and β-naphthylamine combine with diazo-salts in the position indicated by the cross.



Whereas diazo-salts only enter once into the molecule of β-naphthol, α-naphthol combines with two molecules to form a "disazo-compound." In the compound thus formed the second azo-group enters in position (2), forming a substance of the formula



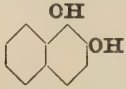
In many respects these "disazo-compounds" are similar to the substantive cotton dyes derived from benzidine and described on p. 70.

As in the benzene series, the orthoamidoazo-compounds of the naphthalene series are of importance only as dyestuffs, the amido-group being incapable of further diazotisation.

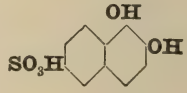
The amido-group in the paraamidoazo-compounds can be further diazotised, and these are therefore largely used for the preparation of dyestuffs containing more azo-groups.

They are themselves, however, of little use as dyestuffs, since they are readily acted upon by acids and alkalies with alteration of the colour.

Both β-naphthohydroquinone



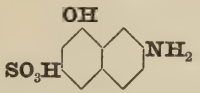
and its sulphonic acid



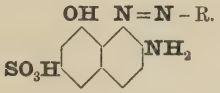
form azo-dyestuffs with diazo-salts.

The amidonaphthol sulphonic acids in many cases react in different ways with diazo-salts, according as the coupling is carried out in acid or alkaline solution.

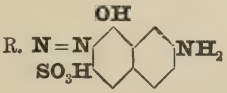
Thus, for example, γ-amidonaphthol sulphonic acid



gives in acid solutions an azo-compound of the formula

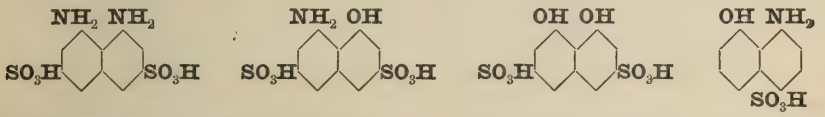


whereas in alkaline solution the compound



is formed.

If, however, in this case, the combination of one molecule of diazo-compound has been effected (whether in acid or alkaline solution), it is impossible to introduce a second molecule of the diazo-compound. Such a formation of a disazo-dyestuff is, however, easily brought about in the case of the 1 : 8 acids, *e.g.* :—

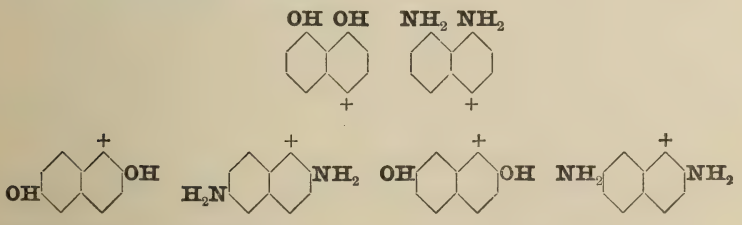


All these react with two molecules of a diazo-salt, which combine in the position adjacent to the NH_2 or OH group in each case.

Diamido-, dioxy-, and oxyamidonaphthalenes and their sulphonic acids react in the following way with diazo-salts.

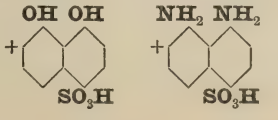
The position into which the azo-group enters is in each case marked with a cross.

1 : 8-diamido- or dioxynaphthalene

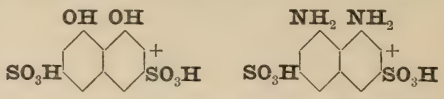


in acid or alkaline solution.

1 : 8-diamido- or dioxynaphthalene 4-sulphonic acid



1 : 8 diamido- or dioxynaphthalene-3 : 6-disulphonic acid



The conditions are various in the case of the amidonaphthol sulphonic acids.

Bülow (*Chem. Ztg.*, xix. 1011) divides them into the following classes :—

(1) Such as are either incapable of being coupled at all, or, if so, only under special conditions.

To these belong the sulphonic acids of the 1 : 2 and 2 : 1 amidonaphthols.

(2) Such as are readily coupled and invariably yield the same product, *e.g.* :—

1 : 8-amidonaphthol-5 : 7-disulphonic acid.

(3) Such as give orthoamidoazo-compounds in acid solution, and ortho-oxyazo-dyestuffs in alkaline solution, *e.g.* :—

1 : 8-amidonaphthol-3 : 6-disulphonic acid (H acid) ;

2 : 8-amidonaphthol-6-sulphonic acid (γ acid) ; and

2 : 5-amidonaphthol-7-sulphonic acid.

Some of them—for example, 1 : 8-amidonaphthol 4- and 5-sulphonic acids—yield "disazo-dyestuffs" in alkaline solution.

III. Abnormalities.—The reaction between diazo-salts and phenols or amines sometimes pursues an abnormal course.

(1) Thus when diazobenzene chloride reacts with aniline, the product does not consist of a true amidoazo-compound, but, owing to the chlorine of the diazo-salt interacting with a hydrogen of the amido-group, a diazoamido-compound is formed according to the equation

$$C_6H_5N_2Cl + H\,HNC_6H_5 \rightarrow C_6H_5N : N.NHC_6H_5 + HCl.$$

The same behaviour is exhibited by *o*-toluidine and by *m*- and *p*-xylidine.

Diazoamidobenzene can, as Kekulé found, be readily converted into amido-azobenzene by heating it with aniline and aniline hydrochloride, the reaction proceeding according to the equation

$$C_6H_5N : N\,NHC_6H_5 + H\,C_6H_4NH_2 \rightarrow C_6H_5N : N.C_6H_4NH_2 + C_6H_5NH_2.$$

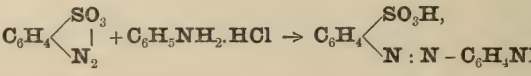
The formation of diazoamido-compounds during the diazotisation of amines can usually be prevented by using a slightly acidified solution of nitrite.

(2) Phenols containing nitro groups, and therefore of a strongly acid character, react in a similar way with diazo-salts.

Thus picric acid, $C_6H_2(NO_2)_3OH$, combines with diazobenzene chloride to form the diazooxy-compound of the formula

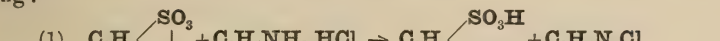
$$C_6H_5N : N.O.C_6H_2(NO_2)_3.$$

(3) The interaction of diazo-sulphanilic acid and aniline hydrochloride proceeds to a certain extent normally with the formation of the true amidoazo-compound



At the same time, however, a curious molecular rearrangement takes place with the formation of amidoazobenzene.

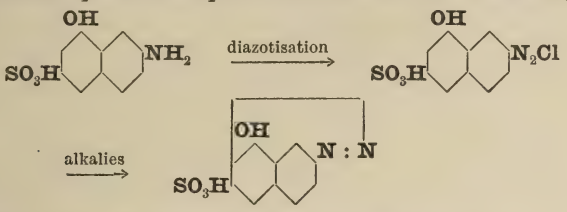
The equations representing the abnormal reaction are evidently the following:—



(2) $C_6H_5N_2Cl + C_6H_5NH_2 \rightarrow C_6H_5N : N.C_6H_4NH_2.HCl.$

(4) In the case of some derivatives of the amidonaphthols, an internal formation of azo-compounds can be brought about by treating the diazo-salt with alkalies.

Thus 2 : 8-amidonaphthol-6-sulphonic acid reacts in the following way:—



IV. Constitution.—The constitution of the azo-compounds is mainly determined by their behaviour on reduction.

When treated with nascent hydrogen they split up at the point of union of the two nitrogen atoms forming one molecule of the base from which the azo-compound was derived, and one molecule of the amido-derivative of the second component containing the amido-group in the position formerly occupied by the azo-group.

Thus amidoazobenzene gives, on complete reduction, aniline and *p*-phenylenediamine

This property, which is taken advantage of in the analysis of the azo-dyestuffs, will be found more fully described on p. 334.

The action of concentrated sulphuric acid on the azo-compounds produces characteristic colours, which are apparently dependent upon the constitution.

These colours are the same as those formed by the action of concentrated sulphuric acid on the azo-hydrocarbon which is the basis of the dyestuff.

Thus azobenzene, $C_6H_5N : N.C_6H_5$, dissolves in concentrated sulphuric acid, giving a brownish-yellow solution, and the same coloration is produced by the action of the concentrated acid in both amidoazobenzene, $C_6H_5N : N.C_6H_4NH_2$, and oxyazobenzene, $C_6H_5N : N.C_6H_4OH$.

α-Azonaphthalene, $C_{10}H_7N : N.C_{10}H_7$, dissolves in concentrated sulphuric acid, forming a blue solution, and the same coloration is produced by its oxy- and amido-derivatives.

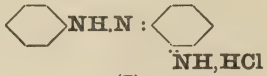
In azo-dyestuffs containing both a benzene and a naphthalene ring, the behaviour towards concentrated sulphuric acid is the same. The presence of a sulphonic acid group, however, causes the substance to give different colorations according as the sulphonic acid group is in the benzene or naphthalene ring.

Thus benzene-azo-β-naphthol, $C_6H_5N : N - C_{10}H_6(OH)\beta$, gives a red-violet coloration with concentrated sulphuric acid, presumably that of the azo-hydrocarbon, $C_6H_5N : N.C_{10}H_7$. The same colour is produced when a sulphonic acid group is contained in the benzene ring. If, however, this group is in the naphthalene ring a yellow coloration is produced; that is to say, the same as is formed by the action of sulphuric acid on azobenzene.

With the polyazo-dyestuffs similar characteristic colours are produced. For example:—

The azo-dyestuffs from	give
Amidoazobenzene sulphonic acids + β-naphthol	green.
Amidoazobenzene and homologues + β-naphthol sulphonic acids	red-violet.
Amidoazobenzene sulphonic acids + β-naphthol sulphonic acids	blue.

The question as to whether the azo-dyestuffs are true azo-compounds or possess the quinone-hydrazone constitution has given rise to many investigations. Evidence has been obtained, on one side or the other, from both chemical and spectroscopical observations and the constitution cannot, perhaps, be regarded as finally settled. There is, however, a marked difference in behaviour between those compounds which have the auxochrome groups in the ortho position to the coupling nitrogen atoms and those which have these groups in the para position. Thus the *o*-amidoazo compounds are not diazotisable but are dyes; the *p*-compounds are diazotisable but are not efficient dyes. Assuming, as is justifiable, that the capacity for a compound to act as a dye is dependent on the dissociation of its salt in solution, it is reasonable to suppose that the non-diazotisability of the *o*-compounds and the dyeing capacity of their salts is due to their having the quinone structure (I) whereas the diazotisability of the *p*-compounds and the



(I)

(II)

stability of their salts is due to their possessing the true azo structure (II).

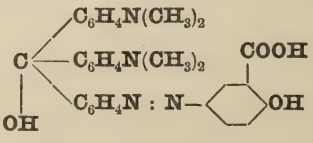
V. The influence of groups and constitution upon the colour of azo-compounds.—The simplest azo-dyestuffs are yellow. Either by the increase in the number of chromophore groups, or by the increase in molecular weight, the colour deepens, passing either through red to violet or into brown.

Azo-dyestuffs which contain only benzene rings are mostly yellow, orange-yellow, or brown.

By the entrance of naphthalene nuclei reds are formed, and azo-dyestuffs containing only naphthalene rings are violet, blue, or black.

Mordant dyestuffs forming green lakes with chromium salts are formed by coupling salicylic acid with the diazo-salts derived from certain compounds of the triphenylmethane series.

Thus azo-green [By] is *m*-amidotetramethyldiamidotriphenylcarbinol azo-salicylic acid

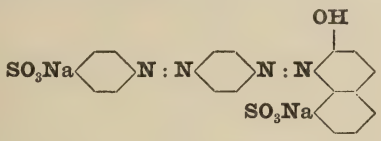


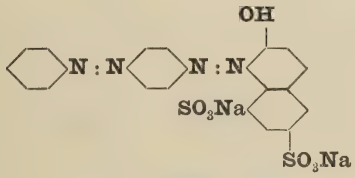
The sulphonic acid group entering into the molecule of an azo-dyestuff does not appreciably alter the nature of the colour; it naturally, however, not only increases the solubility of the compound in water, but also causes it to become an acid dyestuff forming stable salts with alkalies.

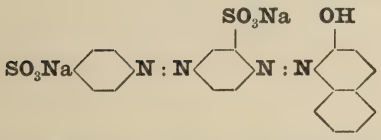
The introduction of sulphonic acid groups is sometimes effected in the finished dyestuff, but more usually they are present in the components which form the azo-compound.

The position of this group is not altogether without influence on the colour of

the dyestuff, as is shown by comparing the three isomeric compounds given below, which give three distinct shades of red :—

(1)  Crocein scarlet.

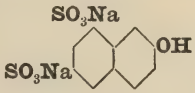
(2)  Brilliant crocein.

(3)  Biebrich scarlet.

The influence of the position of the sulphonic acid group on the colour of the azo-compounds is clearly seen when the azo-dyestuffs derived from the two β-naphthol sulphonic acids 2 : 3 : 6 and 2 : 6 : 8 are compared.

These sulphonic acids (or rather their sodium salts) are termed R and G salt respectively

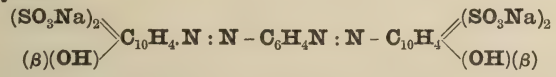
R salt.


G. salt

the letter R (*roth* = red) indicating that red shades of colour are produced, the letter G (*gelb* = yellow) meaning that the azo-dyestuff containing this salt is yellowish-red in colour.

The position of the two azo-groups in the coupling benzene ring contained in these tetrazo-bodies has a most marked influence on the colour of the compound.

Thus the dyestuff



is blue when the two azo-groups are in the para-position; red when they are in the meta-position.

The influence of the auxochrome groups OH and NH_2 upon the colour of the azo-dyestuffs is clearly shown in the benzidine series (see *Substantive cotton dyes*, p. 70).

Tetrazobenzidine[1] salts combined with amidonaphthalene sulphonic acids

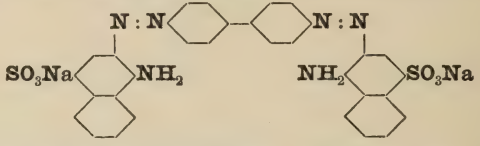
[1] By tetrazobenzidine salt is understood a tetrazo-salt of diphenyl, *e.g.*

which is, of course, derived from benzidine. This nomenclature is more customary than the more correct one, which, as in the case of the name "diazobenzene chloride," indicates the hydrocarbon from which the diazo-salt is derived.

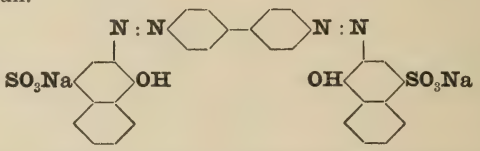
yield red dyestuffs, with naphthol sulphonic acids blue dyestuffs, and in mixed combination (see p. 70) with both naphthylamine and naphthol sulphonic acids dyestuffs which are a mixture of red and blue, *i.e.* violet.

Thus:—

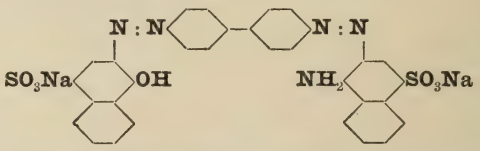
Tetrazobenzidine chloride + naphthionic acid (Na salt) give Congo red



Tetrazobenzidine chloride + Nevile and Winther's acid (Na salt) give a reddish-blue dyestuff.

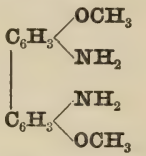


Tetrazobenzidine chloride + 1 mol. naphthionic acid and 1 mol. Nevile and Winther's acid give Congo Corinth (violet) [1]



The entrance of quite indifferent groups—such as, for example, the methoxy-group—frequently has a marked influence on the colour.

Thus dyestuffs derived from dianisidine

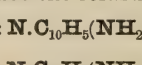


are very much bluer than those from benzidine using the same second component.

SUBSTANTIVE COTTON DYES.

Up to the year 1885 it was always necessary to put the cotton fibre through a preparatory treatment before the artificial dyestuffs could be applied to it. In that year the "Actiengesellschaft für Anilinfabrikation" in Berlin introduced into commerce the dyestuff Congo, which had been discovered in the previous year by Böttiger, and which possessed the property of affixing itself on to the cotton fibre without the aid of any mordant.

Congo is made by the combination of tetrazobenzidine salts with sodium naphthionate, and therefore possesses the formula



[1] The same difference is well illustrated by the three dyestuffs derived from tolidine in place of benzidine.

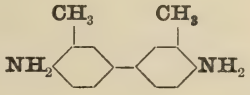
The property of this dyestuff of fixing itself directly on the cotton fibre is apparently due to the presence of the diphenyl residue in its molecule, since other dyestuffs derived in the same way from benzidine and its homologues possess this property. Benzidine is di-*p*-diamidodiphenyl of the formula

and it appears that one condition of the formation of substantive cotton dyestuffs is that the base from which they are derived must be a diamine, since the monoamido-derivatives of diphenyl do not yield azo-compounds substantive to cotton.

Further, the two amido-groups must be in the para-position to the coupling bond, since it has been found that other amido-derivatives of diphenyl do not yield dyestuffs possessing this property.

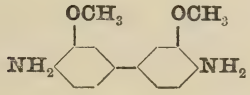
Homologues of benzidine containing the substituting group in the ortho-position to the amido-group also possess this property. Thus

o-tolidine



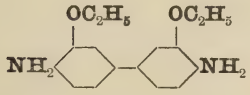
;

dianisidine



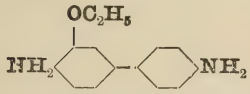
;

diphenetidine



;

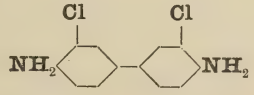
and ethoxybenzidine



are all valuable bases for the preparation of the azo-dyestuffs substantive to cotton.

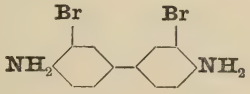
The same applies also to derivatives of benzidine containing halogen groups in the ortho-position to the amido-group. Thus

o-dichlorobenzidine



;

and *o*-dibromobenzidine

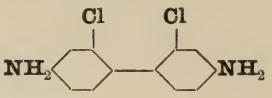


;

yield azo-dyestuffs substantive to cotton.

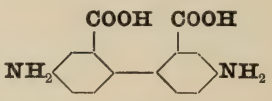
If, however, substituting groups enter the benzidine molecule in the ortho-position to the coupling bond, and therefore in the meta-position to the amido-group, the compounds formed do not yield azo-dyes substantive to cotton.

Thus,
m-dichlorobenzidine



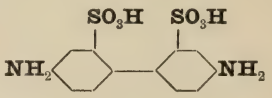
;

m-diamidodiphenic acid



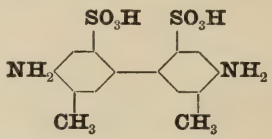
;

benzidine-*m*-disulphonic acid



;

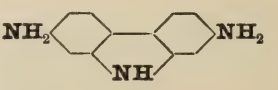
tolidine disulphonic acid



yield azo-compounds which possess no affinity for the vegetable fibre.

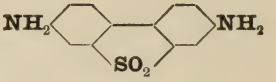
If, however, ring-formation takes place in the ortho-position to the coupling bond, then the bases yield substantive azo-dyestuffs.

Thus,
diamidocarbazol



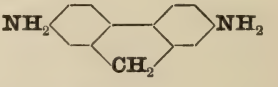
;

benzidine sulphone



;

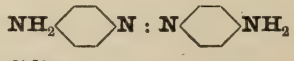
and diamidofluorene



yield azo-dyestuffs substantive to cotton.

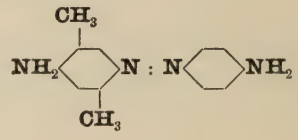
It is not, however, only the derivatives of benzidine and its homologues that yield azo-dyestuffs substantive to cotton. There are a number of other bases which are also para-diamines, but in which the two benzene rings are not directly combined together.

Thus the following bases yield important substantive cotton dyes:—
diamidoazobenzene



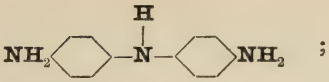
;

p-phenylenediamine-azo-*p*-xylidine

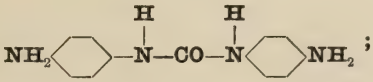


;

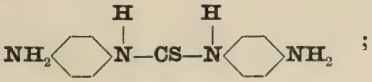
diamidodiphenylamine



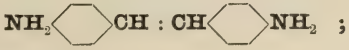
diamidodiphenylurea



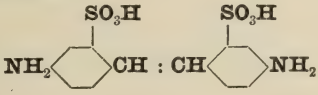
diamidodiphenylthiourea



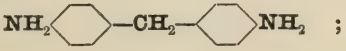
diamidostilbene



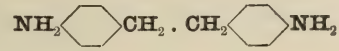
diamidostilbene disulphonic acid



On the other hand :—
p-diamidodiphenylmethane



and *p*-diamidodibenzyl

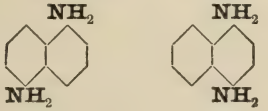


do not yield azo-dyestuffs substantive to cotton.

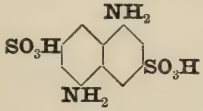
The simplest *p*-diamine, viz., *p*-phenylenediamine

also gives substantive azo-dyestuffs, whereas *m*-phenylenediamine does not.

Also certain diamines in the naphthalene series, as, for example,
1 : 5-diamidonaphthalene, 1 : 4-diamidonaphthalene



and 1 : 5-diamidonaphthalene-3 : 7-disulphonic acid



yield azo-dyestuffs substantive to cotton.

It therefore follows that although a large number of different bases yield azo-dyestuffs which possess the property of directly dyeing the vegetable fibre, yet they all have a very similar constitution.

(1) They are all *p*-diamines.

(2) The amido-groups are in the para-position either to a bond joining two benzene rings, or to the point of juncture of a chain uniting two benzene rings.

(3) This chain is unsaturated.

(4) In the case of derivatives of diphenyl, the ortho-position to the coupling bond must be free.

If this position is occupied, then substantive cotton dyestuffs are only formed when ring-formation takes place between the ortho-position in one benzene ring and that in the other.

There is, however, a characteristic relationship between the colour of the disazo-compounds formed from diamines and their property of dyeing unmordanted cotton, by which it can always be ascertained whether any given base will yield substantive azo-dyestuffs. Those bases which yield these dyestuffs give with naphthol sulphonic acids blue and violet compounds, and with naphthylamine sulphonic acids red dyestuffs.

The isomeric compounds which do not yield substantive cotton dyes give with naphthol sulphonic acids red, and with naphthylamine sulphonic acids orange-yellow dyestuffs.

It must be remembered, however, that the large and important class of substantive dyestuffs which are derived from 2 : 5-diamido-naphthalene-7-sulphonic acid does not fall within this generalisation, and that, so far as their constitutions are known, the substantive dyestuffs of the Primuline group are also exceptions. Moreover, a well-defined substantive colouring matter can be prepared from amidoazobenzenesulphonic acid and nitro-*m*-phenylenediamine.

HISTORICAL.

In 1864 Peter Griess (*Ann.*, 1866, cxxxvii. 60) showed that by the action of diazo-compounds upon amines, amidoazo-compounds were formed.

The oxyazo-compounds were first prepared in 1870 by Kekulé and Hidegh (*Ber.*, 1870, iii. 233) by the interaction of diazo-compounds with phenols.

The first azo-dyestuff, amidoazobenzene, had already been prepared by Griess in 1859 (*Ann.*, 1862, cxxi. 262) by the rearrangement of diazoamidobenzene, without, however, his realising the nature of the reaction. It was manufactured in 1863 by Simpson, Moule, and Nicholson under the name of Aniline yellow, and its constitution was determined three years later by Martius and Griess (*Zeitschr.*, 1866, ii. 132).

In 1863 Martius discovered Phenylene brown (Bismarck brown) and introduced its manufacture later. This dyestuff, which was identified by Caro and Griess (*Zeitschr.*, 1867, iii. 278) as triamidoazobenzene, still finds considerable application in the dyeing industry.

Chrysoidine (diamidoazobenzene) was discovered at the end of 1875 by Caro, and immediately afterwards (January 1876) by Witt (*Ber.*, 1877, x. 654), and was technically prepared in 1876 by Williams, Thomas, and Dower of Brentford.

Shortly afterwards Roussin prepared the first azo-dyestuffs from the naphthols, which were introduced into commerce in the spring of 1877 by Poirrier under the names of Orange I. and Orange II.

In 1876 Griess prepared a number of azo-dyestuffs by the interaction of *p*-diazobenzene sulphonic acid on various bases, which, in the same year, were independently prepared by Witt, and later named the Tropäolines. In 1877 Griess patented a large number of azo-dyestuffs in England, amongst others being a yellow dyestuff prepared from diazodinitrophenol and phenol, and which were manufactured by Joseph Storey, of Lancaster, under the name of Lancaster yellow.

The same patent includes the first red azo-dyestuff prepared by the interaction of diazophenol sulphonic acid and β-naphthol.

In 1878 the firm of Meister, Lucius, & Brüning, of Höchst-am-Main, patented the dyestuffs known as Ponceaux and Bordeaux, this being the first instance of the use of the disulphonic acids of the naphthols.

The first (secondary) disazo-dyestuff was Biebrich scarlet, prepared in 1879 by Nietzki (*Ber.*, 1880, xiii. 800, 1838); and the first (primary) disazo-dyestuff was Resorcin brown discovered by Wallach in 1881 (*Ber.*, 1882, xv. 22).

In 1884 Paul Böttiger took out a patent (E.P. 4415[84]) for the preparation of the first substantive cotton dye—Congo red—prepared by the interaction of tetrazobenzidine and sodium naphthionate, a discovery which gave a considerable impetus to the azo-dyestuff industry, and caused the preparation of a vast number of other dyestuffs of similar constitution.

The first satisfactory black azo dyestuff was Naphthol black, discovered in 1885 by Hoffmann and Weinberg (E.P. 9214[85], A.P. 345,901).

In 1887 Green found that Primuline, previously discovered by him, possessed the property of dyeing cotton direct, and that such dyeings could be diazotised on the fibre and developed with various second components, yielding different colours.

This discovery gave rise to the preparation of many azo-compounds containing free amido-groups, which could be diazotised and developed in the same way on the fibre, yielding colours particularly fast to light and washing.

The year 1889 marked the discovery by Gans of the first direct cotton black (Diamine black RO), and this was followed by the many varieties of Columbia black (A).

In 1891 Hoffmann and Daimler prepared the first direct-dyeing green colour (Diamine green).

In recent years considerable advance has been made in the production of insoluble azo-compounds directly on the fibre.

Thus Nitraniline red, prepared by treating cotton impregnated with β-naphthol with a solution of diazo-*p*-nitraniline, is a dyestuff of very considerable importance.

Owing to the great ease with which the azo-colouring matters can be applied to the fibre, the question of their fastness to washing, light, etc., was perhaps formerly, to some extent, overlooked.

The continued use, however, of the faster mordant dyestuffs, Aniline black, and even some of the natural dyestuffs, has stimulated research in the field of azo-dyes, and since about 1894 many new compounds have been pressed into the service of producing dyestuffs particularly distinguished by their powers of withstanding light and the usual reagents.

DIVISION OF THE AZO-DYESTUFFS.

The azo-dyestuffs can be divided into four chief classes:—

(1) Those containing one azo-group—monoazo-dyestuffs.
(2) Those containing two azo-groups—disazo-dyestuffs.
(3) Those containing three azo-groups—trisazo-dyestuffs.
(4) Those containing four azo-groups—tetrakisazo-dyestuffs.

Each chief division can be subdivided into other divisions, thus:—

(1) (*a*) Amidoazo-compounds.
    (*b*) Oxyazo-compounds.
(2) (*a*) Primary disazo-compounds.
    (*b*) Secondary disazo-compounds.
    (*c*) Dyestuffs from tetrazo-salts with two similar or two different molecules of an amine or phenol.
(3) Are not subdivided.
(4) Are usually produced as such on the fibre by development.

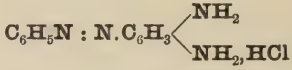
A short description of each subdivision will be found in the following pages, together with one or two examples from each; for a more detailed description of the azo-compounds the reader is referred to larger works on the subject, *e.g.* :— Schultz, *Chemie des Steinkohlentheers*, Band ii.; Green, *Organic Colouring Matters*; Léon Lefèvre, *Matières colorantes artificielles*; or any of the other text-books mentioned on p. 208.[1]

Amidoazo-compounds.—Amidoazobenzene, $C_6H_5N:NC_6H_4NH_2$, which is the simplest amidoazo-compound, is now no longer used in commerce.

It, however, finds considerable application, in the form of its sulphonic acids, in the preparation of certain disazo-dyestuffs to be mentioned later (see *Biebrich scarlet*).

Acid yellow is a mixture of the mono- and disulphonic acids of aniline yellow, and is prepared by treating it with fuming sulphonic acid.

Chrysoidine



is prepared by the interaction of diazobenzene chloride and *m*-phenylenediamine. It still finds considerable application as a dyestuff.

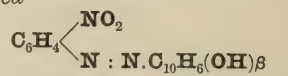
Chrysoidine possesses in a very high degree the property of absorbing the actinic rays of light, which causes it to be considerably used by photographers for the purpose of covering the windows of dark-rooms, etc.

The amidoazo-colours are basic dyestuffs, except in the case of the sulphonic acids, where the entrance of the sulphonic acid group renders them capable of forming salts with alkalies, when they are naturally acid dyestuffs.

Other dyestuffs of this group are :—

Chrysoidine R [H]; [Williams Bros.]	Aniline + *m*-toluylenediamine.
Wool violet S [B] . . .	Dinitraniline + diethyl metanilic acid.
Butter yellow; oil yellow [Williams Bros.]	Aniline + dimethylaniline.
Metanil yellow [B] . . .	Metanilic acid + diphenylamine.
Orange III.	Sulphanilic acid + dimethylaniline.
Orange IV. [B]	Sulphanilic acid + diphenylamine.
Cotton orange G [B] . . .	Primuline + *m*-phenylenediamine disulphonic acid.
Chrome brown P [P] . . .	Picramic acid + *m*-aminophenol.
Palatine chrome brown W [B] .	*o*-Aminophenol-*p*-sulphonic acid + *m*-phenylenediamine.
Sulphone acid blue R [By] . .	H-acid (p. 18) + phenyl-α-naphthylamine-8-sulphonic acid.
Metachrome brown B [A] . .	Picramic acid + *m*-toluylenediamine.

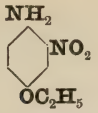
Oxyazo-compounds.—The most important insoluble dyestuff belonging to this group is p-*nitraniline red*



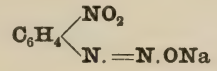
This dyestuff is never introduced into commerce in the finished state, except as a pigment, but is always produced by the dyer directly on the fibre by first treating the cotton fibre with an alkaline solution of β-naphthol, and subsequently either steeping it in, or printing on it, a solution of diazotised *p*-nitraniline.

A similar product is Phenetidine red (M.L.Br.), a bluish-red dyestuff prepared from nitrophenetidine and β-naphthol.

[1] For an account of the azo-colouring matters see also the article under that heading in Thorpe's *Dict. of Applied Chem.*, vol. i. p. 358.



Nitrosamine red, as formerly mentioned (p. 50), is the sodium salt of *p*-nitrobenzene *anti*-diazo-hydroxide



and is prepared by the action of caustic alkali on diazo-*p*-nitraniline chloride.

On treatment with acids it yields a salt of diazo-*p*-nitraniline (*p*-nitrobenzene diazonium chloride), which is then available for the use of the dyer to prepare *p*-nitraniline red (Nitrosamine red).

The nitrosamine paste admixed with β-naphthol can also be printed on the fibre, when, on passing the printed material through dilute acid, the dye will be developed.

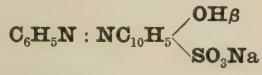
Dyestuffs similar in composition to *p*-nitraniline red can also be prepared by the diazonaphthylamines and from dianisidine.

The soluble oxyazo-compounds are the sodium salts of the various sulphonic acids, and are prepared by combining sulpho-acids of phenol and naphthols with diazo-salts.

The *Ponceaux* are compounds prepared by the interaction of various diazo-salts with the naphthol sulphonic acids.

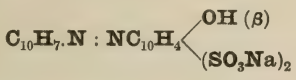
Two typical instances are :—

Ponceau 4GB [A]



prepared from diazobenzene chloride and β-naphthol monosulphonic acid (Schäffer's acid), and

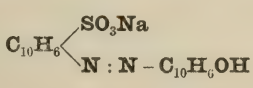
Crystal Ponceau [B], crystal Ponceau 6B [C]



prepared from diazonaphthalene chloride and β-naphthol disulphonic acid G.

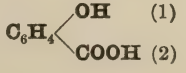
They are acid dyestuffs and are well adapted for the dyeing of wool.

Fast red A [B] is an instance of a dyestuff of this group which contains two naphthalene rings ; it is



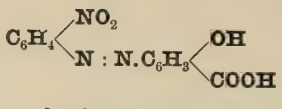
and is prepared from diazo-naphthionic acid and β-naphthol.

There are also certain dyestuffs belonging to this series which are made by the use of salicylic acid

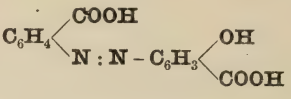


as second component.

Such are :—
Alizarine yellow GG [M]



prepared from *m*-nitraniline and salicylic acid, and
Diamond yellow G [By]

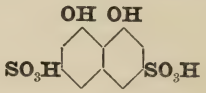


prepared from the diazo-salt of *m*-amidobenzoic acid and salicylic acid.

Owing to the presence of the OH and COOH groups in the ortho-position in the salicylic acid residue, these compounds are mordant dyestuffs, and find considerable application as such in the textile industry.

In this respect, also, the azo-dyestuffs derived from chromotropic acid are interesting.

This acid is 1 : 8-dioxynaphthalene-3 : 6-disulphonic acid



and its sodium salt gives, on combination with diazo-salts, the dyestuffs known as the Chromotropes. Here, again, the *peri*-position of the hydroxyl groups in the chromotropic acid causes the azo-dyestuffs derived from it to form lakes with metallic salts.

They may be applied as follows :—

Wool is dyed red in an acid bath containing a Chromotrope, and, on subsequent treatment with potassium bichromate solution, becomes dark blue to black. The dyeings thus produced are exceptionally fast.

Other dyestuffs of this group are :—

Ponceau 2G [A] . . .	Aniline + β-naphthol disulphonic acid R.
Orange G [A] . . .	Aniline + β-naphthol disulphonic acid G.
Chromotrope 2R [M] .	Aniline + chromotropic acid.
Chromotrope 2B [M] .	*p*-Nitraniline + chromotropic acid.
Alizarine yellow R [By].	*p*-Nitraniline + salicylic acid.
Victoria violet 4BS [M].	Alkaline reduction of Chromotrope 2B.
Chromotrope 6B [M] .	*p*-Amidoacetanilide + chromotropic acid.
Orange GT [By] . .	Toluidine + β-naphthol sulphonic acid S.
Azofuchsine B [By] .	Toluidine + dioxynaphthalene sulphonic acid S.
Azococcine 2R [A] .	Xylidine + α-naphthol sulphonic acid NW.
Palatine scarlet [B] .	*m*-Xylidine + α-naphthol-3 : 6-disulphonic acid.
Brilliant orange R [M] .	Xylidine + β-naphthol sulphonic acid S.
Ponceau 2R [A] . .	Xylidine + β-naphthol disulphonic acid R.
Ponceau 3R [A] . .	ψ-Cumidine + β-naphthol disulphonic acid R.
Palatine red [B] . .	α-Naphthylamine + α-naphthol-3 : 6-disulphonic acid.
Fast red BT [By]. .	α-Naphthylamine + β-naphthol sulphonic acid S.
Fast red B [By] . .	α-Naphthylamine + β-naphthol disulphonic acid R.
Chromotrope 10B [M] .	α-Naphthylamine + chromotropic acid.

Azoeosine [By]	*o*-Anisidine + α-naphthol sulphonic acid NW.
Erika B [A]	Dehydro-thio-*m*-xylidine + α-naphthol-3 : 6-disulphonic acid.
Chrysoïne [B]	Sulphanilic acid + resorcinol.
Orange II. [B]	Sulphanilic acid + β-naphthol.
Azofuchsine G [By]	Sulphanilic acid + dioxynaphthalene sulphonic acid S.
Azorubine [Lev]	Naphthionic acid + α-naphthol sulphonic acid NW.
Fast red [A]	Naphthionic acid + β-naphthol sulphonic acid S.
New coccine [B]	Naphthionic acid + β-naphthol disulphonic acid G.
Chromotrope 8B [M]	Naphthionic acid + chromotropic acid.
Lithol red [B]	β-Naphthylamine-1-sulphonic acid + β-naphthol.
Double brilliant scarlet G [A]	β-Naphthylamine sulphonic acid Br + β-naphthol.
Chrome yellow D [By]	β-Naphthylamine monosulphonic acid Br + salicylic acid.
Crumpsall yellow [Lev]	β-Naphthylamine disulphonic acid G + salicylic acid.
Diamond yellow R [By]	*o*-Amidobenzoic acid + salicylic acid.
Sorbine red [B] Lanafuchsine [C]	*p*-Amidoacetanilide + α-naphthol-3 : 6-disulphonic acid.
Diazine black [K]	Safranine + phenol.
Indoïne blue R [B]	Safranine + β-naphthol.
Diamond black PV [By]	*o*-Amidophenol-*p*-sulphonic acid + 1 : 5-dioxynaphthalene.
Palatine chrome green G [B] Chrome fast green G [I]	4-Nitro-2-amidophenol + 1 : 8-amidonaphthol-3 : 6-disulphonic acid.
Acid alizarin black R [M]	6-Nitro-2-amidophenol-4-sulphonic acid + β-naphthol.
Chrome fast cyanine G [I] Eriochrome blue black B [G]	1-Amido-β-naphthol sulphonic acid + α-naphthol.
Eriochrome black T [G]	8-Nitroamido-β-naphthol-4-sulphonic acid + α-naphthol.
Anthracene chrome black [C]	3-Amido-β-naphthol-7-sulphonic acid + β-naphthol.
Palatine chrome black 6B [B] Eriochrome blue black R [G]	1-Amido-β-naphthol-4-sulphonic acid + β-naphthol.
Lanacyl blue BB [C]	1 : 8-Amidonaphthol-3 : 6-disulphonic acid H + 1 : 5-amidonaphthol.
Rosophenine 10B [Cl Co]	Dehydrothio-*p*-toluidine sulphonic acid + α-naphthol sulphonic acid NW.

Disazo-dyestuffs.—(1) *Primary.*—These are the azo-compounds which are formed by the successive action of two similar or different diazo-salts—obtained by the diazotisation of a monamine—on an amine or phenol, whereby the two diazo-groups enter on different carbon atoms of the phenol or amine used.

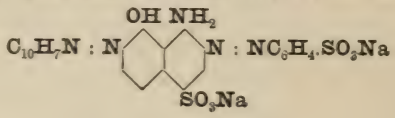
The first example of this class was aniline disazophenol

$$\begin{matrix} C_6H_5N : N \\ C_6H_5N : N \end{matrix} \Big\rangle C_6H_3OH$$

prepared in 1864 by Griess, by the action of potassium carbonate on diazobenzene nitrate, and called by him oxytetrabenzene or phenolbidiazobenzene (*Ann.*, 1866, cxxxvii. 84).

The following two dyestuffs are typical members of this series, and are of considerable importance:—

Palatine black [B]; *Wool black 4B and 6B* [A]; *Buffalo black* [Sch]

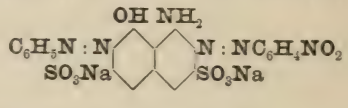


or

Sulphanilic acid
α-Naphthylamine } 1-amido-8-naphthol-4-sulphonic acid

is prepared by treating 1-amido-8-naphthol-4-sulphonic acid first in acid solution with diazotised sulphanilic acid and then in alkaline solution with diazotised *α*-naphthylamine.

Coomassie blue black [Lev]; *Naphthol blue black* [C]



or

p-Nitraniline
Aniline } amidonaphthol disulphonic acid H.

Other dyestuffs of this group are:—

Resorcin brown . . . *m*-Xylidine
Sulphanilic acid } resorcinol.

Chrome patent green N [K] Aniline
Picramic acid } 1-amido-8-naphthol-4 : 6 disulphonic acid.

Benzo fast scarlets [By] . Two mols. of a diazo-compound combined with the product of the action of phosgene on 2-amido-5-naphthol-7-sulphonic acid.

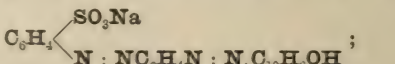
Anthracene acid brown [C] . Sulphanilic acid
p-Nitraniline } salicylic acid.

(2) *Secondary.*—These are compounds made by the combination of diazotised amidoazo-dyestuffs with amines and phenols.

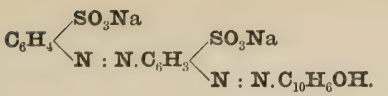
The series contains many important dyestuffs, which find their application in the dyeing of wool and cotton.

The following are typical examples:—

Biebrich scarlet.—This dyestuff is prepared from the diazo-compound of Acid yellow combined with *β*-naphthol. It therefore consists of two compounds, one made from the monosulphonic acid of Aniline yellow, and having the formula

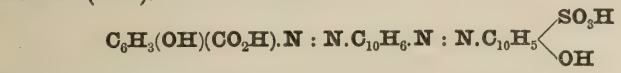


and another made from the disulphonic acid and having the composition



The disulphonic acid, however, usually predominates.

Diamond black F [By]; *Era black F* [Lev]; *Fast Chrome black B* [Sch].—*p*-Amidosalicylic acid is diazotised and combined with α-naphthylamine, and the aminoazo-dyestuff thus produced is diazotised and combined with α-naphthol-4-sulphonic acid (NW). The constitution is



Other dyestuffs of this series are :—

Sudan III.	Amidoazobenzene + β-naphthol.
Brilliant crocein M [C] .	Amidoazobenzene + β-naphtholdisulphonic acid G.
Cloth red B [By] . . .	Amidoazotoluene + α-naphthol sulphonic acid NW.
Crocein 3B [Sch] . . .	Amidoazotoluene + α-naphthol disulphonic acid Sch.
Wool red B [C] . . .	Amidoazotoluene + β-naphthol disulphonic acid R.
Bordeaux BX [By] . .	Amidoazoxylene + β-naphthol sulphonic acid S.
Union fast claret [Lev] .	Amidoazoxylene + β-naphthol disulphonic acid R.
Ponceau 4RB [A] . .	Amidoazobenzene sulphonic acid + β-naphthol 8-sulphonic acid.
Crocein scarlet O extra [K] .	Amidoazobenzene disulphonic acid + β-naphthol 8-sulphonic acid.
Crocein scarlet 8B [By] .	Amidoazotoluene sulphonic acid + β-naphthol 8-sulphonic acid.
Sulphon cyanine [By]; Tolyl blue [M] . . .	Metanilic acid-azo-α-naphthylamine + phenyl-α-naphthylamine-8-sulphonic acid.
Naphthylamine black D [C]; Coomassie wool black D [Lev]; Buffalo black AD [Sch]	α-Naphthylamine disulphonic-acid-azo-α-naphthylamine + α-naphthylamine.
Naphthol black 6B [C] .	α-Naphthylamine disulphonic acid-azo-α-naphthylamine + β-naphthol disulphonic acid R.
Naphthol black B [C] . .	β-Naphthylamine-6 : 8-disulphonic acid-azo-α-naphthylamine + β-naphthol disulphonic acid R.
Diamond green [By] . .	Amidosalicylic acid-azo-α-naphthylamine + dioxynaphthalene monosulphonic acid S.
Coomassie wool black R [Lev]	Acetyl-*p*-phenylenediamine-azo-α-naphthylamine + β-naphthol sulphonic acid S. (The final product hydrolysed.)
Coomassie wool black S [Lev].	Like the preceding, except that β-naphthol disulphonic acid R is used as the final component.
Diaminogen black [C] (for cotton) . . .	Acetyl-1 : 4-naphthylenediamine 6 or 7 sulphonic acid-azo-α-naphthylamine + amidonaphthol sulphonic acid γ. (The final product hydrolysed.)
Diaminogen blue BB [C] .	Like the preceding, except that β-naphthol sulphonic acid S is used as the final component.
Nerol B [A] . . .	p-Amidodiphenylamine-*o*-sulphonic acid-azo-α-naphthylamine + β-naphthol disulphonic acid R.

Dyestuffs from tetrazo-salts are prepared by combining a tetrazo-salt obtained from a primary diamine, with two similar or different amines or phenols. The most important members of this class are those which are derived from benzidine and its homologues, which, as previously mentioned, possess the property of directly dyeing the cotton fibre.

The formation of the disazo-dyestuff is brought about in the usual way. The diamine is treated with nitrous acid and converted into the tetrazo-salt, a process which, in the case of benzidine and its homologues, proceeds very smoothly.

The only difference, then, between the formation of the azo-compound and the disazo-compound is that in the case of the latter two molecules of the amine or phenol used as second component have to be employed.

The formation of the disazo-dyestuffs takes place in two distinct stages. In the first place, one molecule of the second component combines with the tetrazo-salt, forming a well-defined intermediate product which still contains a free diazo-group.

These intermediate products may be in most cases isolated, and are well-characterised, often crystalline, compounds.

By boiling with water the diazo-group is replaced by hydroxyl, and dyestuffs are formed which are, however, of little technical value.[1]

If the intermediate product is further combined with another molecule of the same amine or phenol, the simple benzidine dyestuffs are produced, and if a molecule of some other amine or phenol is employed, the mixed benzidine colours are formed. Thus:—

Tetrazobenzidine chloride

$$\begin{matrix} C_6H_4N_2Cl \\ | \\ C_6H_4N_2Cl \end{matrix}$$

combines immediately with 1 mol. of sodium naphthionate in acid solution to form the intermediate compound

$$\begin{matrix} C_6H_4N : N - C_{10}H_5\begin{matrix}NH_2 & (1)\\ SO_3H & (4)\end{matrix} \\ | \\ C_6H_4N_2Cl. \end{matrix}$$

This diazo-salt, on combination with a further molecule of sodium naphthionate, yields the acid of which *Congo red* is the sodium salt

$$\begin{matrix} C_6H_4N : N.C_{10}H_5\begin{matrix}NH_2 & (1)\\ SO_3Na & (4)\end{matrix} \\ | \\ C_6H_4N : N.C_{10}H_5\begin{matrix}NH_2 & (1)\\ SO_3Na & (4)\end{matrix} \end{matrix}$$

The entrance of the second molecule of the second component takes place, however, slowly, and in some cases it is necessary to allow two to three days to elapse before combination is complete.

If the above intermediate compound is combined (in alkaline solution) with, for example, 1 mol. of Nevile and Winther's acid (1 : 4-naphthol sulphonic acid), a mixed benzidine dyestuff—*Congo Corinth*—is produced

$$\begin{matrix} C_6H_4N : N.C_{10}H_5\begin{matrix}NH_2 & (1)\\ SO_3Na & (4)\end{matrix} \\ | \\ C_6H_4N : N.C_{10}H_5\begin{matrix}OH & (1)\\ SO_3Na & (4)\end{matrix} \end{matrix}$$

[1] With the exception, however, of Diamond flavine.

A variety of bases used in the preparation of the substantive cotton dyes have been already mentioned on pp. 59 *et seq.*, and it is easy to understand that these bases, both in mixed and simple combination with the large number of naphthol- and naphthylamine-sulphonic acids available for the purpose, render the number of the azo-dyestuffs substantive to cotton, which have been prepared and which are in daily use, very considerable indeed.

The following list gives the more important disazo-dyestuffs derived from the *p*-diamines:—

Diamine fast red F [C]; Dianol fast red F [Lev]; Direct fast red F [Sch] — Benzidine — salicylic acid. / γ-amidonaphthol sulphonic acid (in acid solution).

Chrysamine G; Direct yellow C G [Sch] — Benzidine — salicylic acid. / salicylic acid.

Benzopurpurine 4B: Direct red 4B [Sch] — Tolidine — naphthionic acid. / naphthionic acid.

Benzopurpurine B — Tolidine — β-naphthylamine sulphonic acid Br. / β-naphthylamine sulphonic acid Br.

Dianol brilliant red [Lev]; Diphenyl red 8B [G] — Dichlorobenzidine — β-naphthylamine-3 : 6-disulphonic acid. / β-naphthylamine-3 : 6-disulphonic acid.

Benzocyanine R [By] — Benzidine — amidonaphthol disulphonic acid H. / amidonaphthol sulphonic acid S.

Diamine blue BX [C]; Benzo blue BX [Lev]; Niagara blue BX [Sch] — Tolidine — α-naphthol sulphonic acid NW. / amidonaphthol disulphonic acid H.

Benzoazurine G [Lev]; Direct blue G extra [Sch] — Dianisidine — α-naphthol sulphonic acid NW. / α-naphthol sulphonic acid NW.

Cotton yellow G [B] — Di-*p*-amidodiphenylurea — salicylic acid. / salicylic acid.

Diamine brown M [C]; Crumpsall direct fast brown B [Lev]; Direct brown 3RB [Sch] — Benzidine — salicylic acid. / amidonaphthol sulphonic acid γ (alkaline solution).

Milling scarlet [M] — 4 : 4′-Diamido-2 : 2′-dimethyldiphenylmethane + 2 mols. α-naphthol-5-sulphonic acid.

Benzo violet R [By] . Benzidine → α-naphthol sulphonic acid NW. + α-naphthol-3 : 6-disulphonic acid.

Diamine black BH [C]; Diazine black H extra [Sch] → Benzidine → amidonaphthol sulphonic acid γ. + amidonaphthol disulphonic acid H.

Benzopurpurine 10B [By]; Buffalo cardinal 7B [Sch] → Dianisidine → naphthionic acid. + naphthionic acid.

Chicago blue 6B [A]; Dianol brilliant blue 6B [Lev] → Dianisidine → 2 mols. of 1 : 8-amidonaphthol-2 : 4-disulphonic acid.

Diamine sky blue; Niagara blue 4B [Sch]; Chlorazol blue 6G [H] → Dianisidine → amidonaphthol disulphonic acid H. + amidonaphthol disulphonic acid H.

Palatine chrome black F [B] → 2 : 6-Diamidophenol-4-sulphonic acid → β-naphthol. + β-naphthol.

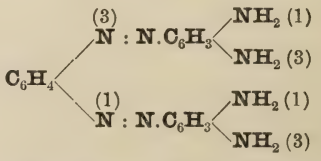
Chrysophenine G . . → Diamidostilbene disulphonic acid → phenetol. + phenetol.

Dianthine [Claus & Co]; Rosophenine 4B [Cl Co] → Diamidoazoxytoluene → α-naphthol sulphonic acid NW. + α-naphthol sulphonic acid NW.

Acid anthracene red 3B [By] → *o*-Tolidine disulphonic acid → β-naphthol. + β-naphthol.

Bismarck brown is derived from *m*-phenylenediamine on treatment with nitrous acid. It is one of the oldest azo-dyestuffs, having been discovered in 1863 by Martius, and prepared technically by Roberts, Dale & Co. in 1866.

It is formed by the combination of 2 mols. of *m*-phenylenediamine with tetrazo-*m*-phenylenediamine, and therefore has the formula



It is a basic dyestuff, dyeing wool a red-brown shade. It has no affinity for the cotton fibre, and can only be affixed to it with the aid of tannin.

Trisazo-dyestuffs.—These dyestuffs can be prepared by a variety of methods, one of which consists in so arranging that one of the second components in a benzidine colour contains a diazotisable amido-group. Thus :—

Direct black V [S] is

Benzidine → amidonaphthol sulphonic acid γ.
Benzidine → 7-amido-α-naphthol-3 : 6-disulphonic acid + α-naphthylamine.

Diamine bronze G [C] is

Benzidine → salicylic acid.
Benzidine → amidonaphthol sulphonic acid H + *m*-phenylenediamine.

Trisulphone brown B [S] is

Benzidine → salicylic acid.
Benzidine → 2-amido-8-naphthol-3 : 6-disulphonic acid + *m*-phenylenediamine.

Benzo fast blue B [By] is

Dianisidine → α-naphthol-3 : 8-disulphonic acid.
Dianisidine → α-naphthylamine + α-naphthol-3 : 8-disulphonic acid.

Another method for the preparation of these dyestuffs consists in allowing a diazo-salt to react on one of the components of a benzidine dyestuff. Thus :—

Diamine green G [C]; *Dianol green* G [Lev]; *Chlorazol green* G [H]; *Erie direct green* MT, BT [Sch] is

Benzidine → salicylic acid.
p-Nitraniline → amidonaphthol disulphonic acid H.

Congo brown G [A]; *Direct brown* GR [Sch] is

Benzidine → salicylic acid.
Sulphanilic acid → resorcinol.

Columbia green [A] is

Benzidine → salicylic acid.
Sulphanilic acid → amidonaphthol sulphonic acid 1 : 8 : 4.

Other dyestuffs of this group are :—

Chloramine black N [S]

Benzidine → *m*-phenylenediamine.
Benzidine → 2 : 5-dichloroaniline + amidonaphthol disulphonic acid H.

Erie direct black GX [Sch]; Direct deep black EW extra [By]

Benzidine → *m*-phenylenediamine.
Aniline → amidonaphthol disulphonic acid H.

Diamine black HW [C]; Ingrain black G [H]

Benzidine / *p*-Nitraniline → amidonaphthol sulphonic acid γ. / amidonaphthol disulphonic acid H.

Alizarine yellow FS [DH] . . Magenta + salicylic acid.

Columbia black FB, FF extra [A]; Dianol black, FB, FF [Lev]; Panama black, R, F [Sch]

p-Phenylenediamine → α-naphthylamine sulphonic acid (Cleve). / amidonaphthol sulphonic acid γ + *m*-phenylenediamine.

Tetrakisazo-dyestuffs.—For the most part, the dyestuffs of this group are produced directly on the fibre by the diazotisation and development of material dyed with some substantive cotton dye containing two diazotisable amido-groups.

The colours produced are known as "Ingrain colour," and the method was first introduced by Green, who applied it to Primuline (see p. 172).

There are, however, a few dyestuffs of this group which are introduced into commerce in the finished state.

Benzo brown G [By]

Sulphanilic acid / *m*-Phenylenediamine / Sulphanilic acid → *m*-phenylenediamine. / *m*-phenylenediamine.

prepared from Bismarck brown by treatment with two molecules of diazosulphanilic acid; and

Hessian brown BB [L]

Sulphanilic acid / Benzidine / Sulphanilic acid → resorcinol. / resorcinol.

Direct brown J [I]

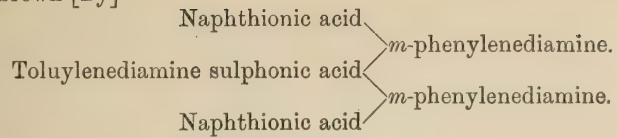
m-Amidobenzoic acid / *m*-Phenylenediamine / *m*-Amidobenzoic acid → *m*-phenylenediamine. / *m*-phenylenediamine.

Other dyestuffs of this group are:—

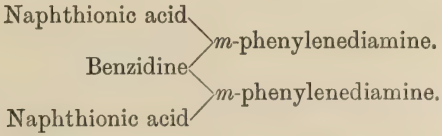
Anthracene acid brown B [C]

Nitroamidosalicylic acid / *m*-Phenylenediamine / Nitroamidosalicylic acid → α-naphthylamine. / α-naphthylamine.

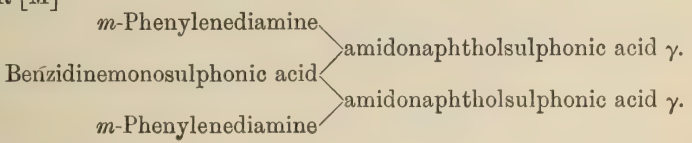
Toluylene brown [By]



Cotton brown A [C]



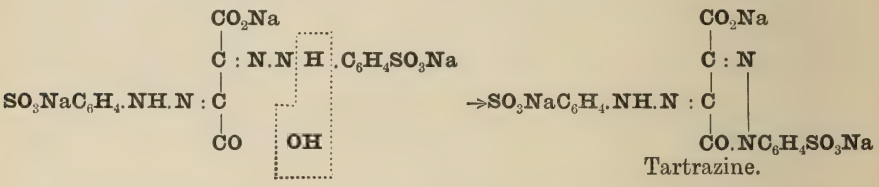
Dianil black PR [M]



CHAPTER XII.

PYRAZOLONES.

The most important dyestuff of this series is *Tartrazine*, which was discovered by Ziegler in 1884 (*Ber.*, 1887, xx. 834), who prepared it by the action of phenylhydrazine sulphonic acid on sodium dioxytartrate. He considered it to be a hydrazone, but Anschütz (*Ann.*, 1897, ccxciv. 219) showed that it was a pyrazolone derivative, its formation being represented by the scheme

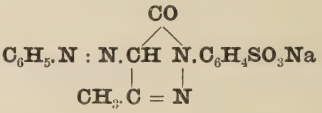


Tartrazine.

It is also prepared by condensing 1 mol. of phenylhydrazine sulphonic acid with ethyl oxalacetate, treating the product with diazotised sulphanilic acid and hydrolysing the resulting ester.

Tartrazine is a handsome yellow wool dye, extremely fast to light, in which respect few other dyestuffs are superior to it.

Fast Light Yellow G [By], *Flavazine* L [M], prepared by the action of diazotised aniline on 1-*p*-sulphophenyl-3-methyl-5-pyrazolone, has the formula



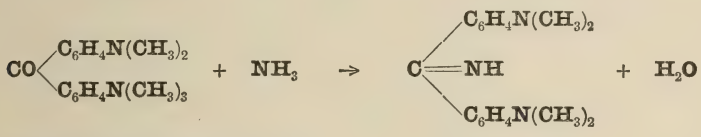
The *Xylene yellows* [KS] are prepared by treating 1-*o*-*m*-dichlor-*p*-sulphophenyl - 3 - methyl - 5 - pyrazolone with diazo - compounds such as diazotised sulphanilic acid, and the combination of diazotised primulinesulphonic acid with phenylmethylpyrazolone and its derivatives gives rise to the *Dianil yellows* [M]. From the latter pyrazolone and diazotised 1-amido-2-naphthol-4-sulphonic acid *Eriochrome red* B [G] is obtained. (For a full account of these dyestuffs see Cohn, *Die Pyrazolonfarbstoffe*, Stuttgart, 1910.)

CHAPTER XIII.

AURAMINE.

H. Caro and A. Kern in 1883 (E.P. 5512[84]) prepared a dyestuff by fusing tetramethyldiamidobenzophenone with ammonium chloride and zinc chloride at 150–160°, which was introduced by the Badische Anilin und Soda Fabrik under the name of Auramine.

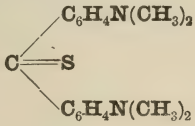
Its method of preparation can be represented by the following equation :—



tetramethyldiamidobenzophenone. Auramine base.

At the present day, however, this dyestuff is prepared by a method suggested by Sandmeyer in 1889 (E.P. 12,549[89], and 16,666[90]), which consists in heating tetramethyldiamidodiphenylmethane with sulphur, ammonium chloride, and common salt in a current of ammonia gas.

In this reaction the thioketone



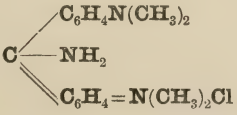
is formed as an intermediate product.

Auramine is a basic wool dyestuff or tannin cotton dye, and is most frequently met with as its hydrochloride. It is exceptionally fast to light, but, unfortunately, is readily hydrolysed by boiling water. Hence in its use care must be taken not to allow the dye-bath to exceed a temperature of 60–70° C.

It is in its properties closely allied to the compounds of the triphenylmethane series to be mentioned later.

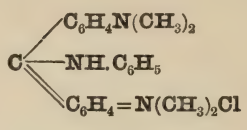
Thus, on reduction, it is converted into a "*leuco*" or colourless compound, which is retransformed into the dyestuff on oxidation.

The constitution of the Auramine base given above is that suggested by Graebe. Stock (*J. prak. Chem.*, 1893, xlvii. 401), however, considers that the quinone structure represented by the formula



best represents the constitution of Auramine hydrochloride.

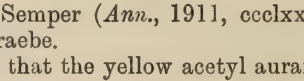
He bases his opinion upon the presence of an imino-group in phenyl-auramine hydrochloride



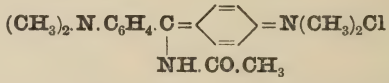
This formula represents Auramine hydrochloride as a triphenylmethane derivative, in which one of the phenyl groups has been replaced by an amido-group.

Recent researches by Semper (*Ann.*, 1911, cccIxxxi. 234) support, however, the original formula of Graebe.

He finds, for example, that the yellow acetyl auramine



gives deep-violet or bluish-green salts totally distinct from those of Auramine itself. The properties of the salts of the acetyl derivative show them to possess a quinonoid structure

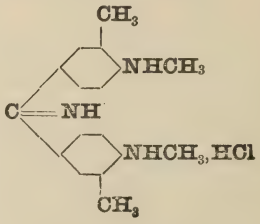


and the change from yellow imino form to the strongly coloured salt is so sharp that the substance can be used as an indicator.

It therefore follows that the yellow salts of Auramine cannot have the quinonoid structure.

Auramine G [B] is prepared by heating sym-dimethyldiamido-di-*o*-tolyl-methane with sulphur in a current of ammonia gas.

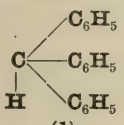
Its constitution is represented by the formula

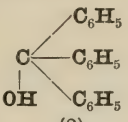


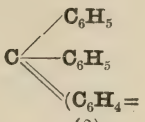
CHAPTER XIV.

TRIPHENYLMETHANE DYESTUFFS.

The hydrocarbon triphenylmethane (1)


(1)


(2)

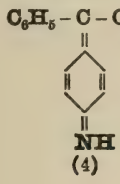

(3)

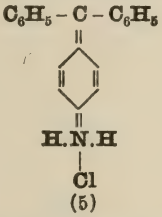
is the basis of a large number of important dyestuffs, which can all be considered as anhydro-derivatives of triphenylcarbinol (2).

These dyestuffs are the salts of the bases or acids formed by the entrance of amido- or hydroxyl groups into the molecule of triphenylcarbinol, which salt-formation always takes place with elimination of water and formation of the quinone ring (3) (see p. 87). One, two, or three amido- or hydroxyl groups may enter, but only the di- and tri-derivatives are of importance as dyestuffs.

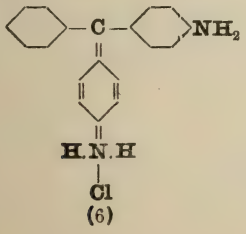
Furthermore, it is necessary that these groups should enter into different benzene rings, and in the para-position to the methane carbon atom.

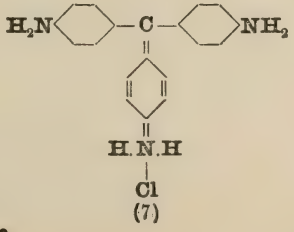
It is convenient to regard the colouring matters of this series as basic derivatives of Fuchsonimine or hydroxylic derivatives of Fuchsone in the manner suggested by v. Baeyer. Fuchsonimine (4) is a coloured substance, forming orange-red salts (5), which can only be used for the dyeing of tannined cotton


(4)

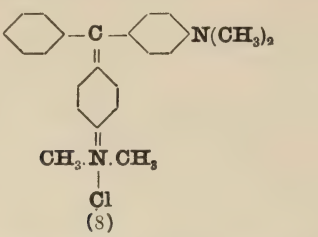

(5)

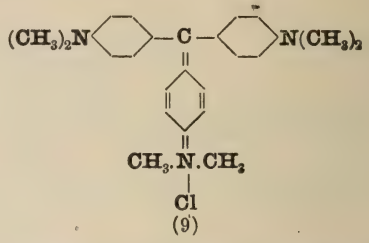
By the entrance of one amido-group in the para-position to the methane carbon atom in one of the phenyl groups, the first true dyestuff of the series, Döbner's violet (6) is produced, and the entrance of a further amido-group in the para-position of the remaining benzene nucleus leads to the bluish-red para-rosaniline (7)


(6)

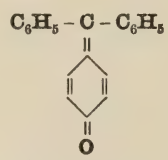

(7)

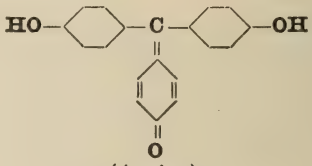
The alkylation of the amido-groups in these compounds then leads to substances of different shades of colour depending on the number and nature of the substituting alkyl groups, and of these Malachite green (8) and Crystal violet (9) may be taken as types


(8)


(9)

In the same way the hydroxylic derivatives of the series may be regarded as being derived from Fuchsone by the entrance of hydroxyl groups in the para-positions of the two benzene nuclei, thus :—


(Fuchsone).


(Aurine).

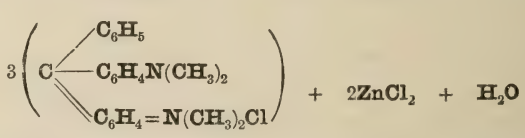
The triphenylmethane dyestuffs will therefore be considered under the following heads :—

(*a*) Those containing two basic groups—The Malachite green series.
(*b*) Those containing three basic groups—The Rosaniline series.
(*c*) Those containing three hydroxyl groups—The Rosolic acid series.

(*a*) The Malachite Green Series.

The older members of this group are green, and it was not until the year 1888 that blue members—the Patent blues—were prepared.

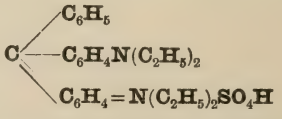
Malachite green often appears in commerce as the zinc chloride double salt of the formula



but more frequently as the oxalate, and is prepared by a method fully described on p. 270.

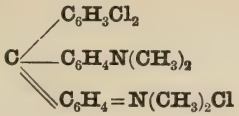
It is one of the oldest of the artificial colouring matters, and was discovered by O. Fischer in 1877 (*Ber.*, 1877, x. 1624), who prepared it by the method used for its commercial production at the present day.

Brilliant green is the corresponding tetraethyl derivative of the formula (sulphate)



Its method of preparation is analogous to that of Malachite green.

New solid green 2B [I]



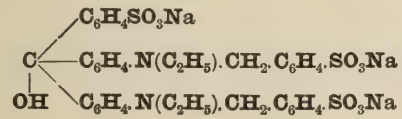
is interesting as showing the influence on the colour of a compound of this series by the entrance of chlorine atoms into the unsubstituted benzene ring. It is prepared from dichlorobenzaldehyde (CHO : Cl : Cl = 1 : 2 : 5) and dimethylaniline, with subsequent oxidation of the leuco-base formed.

The shade of green of this dyestuff is very much bluer than that of Malachite green.

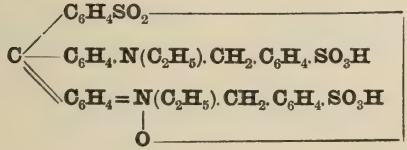
Sulphonic acids of the Malachite green series.—The production of sulphonic acids from members of the triphenylmethane series will be more fully discussed under the head of the sulphonic acids derived from dyestuffs of the Rosaniline series, since these are of more importance than those derived by the sulphonation of dyestuffs of the Malachite green series.

Helvetia green, which is the sodium salt of the sulphonic acid prepared by the direct sulphonation of Malachite green, is no longer manufactured, and has been replaced by the following dyestuff:—

Acid green (GG) [By], or Light green (SF yellowish) [B], prepared by sulphonating the condensation product of benzaldehyde with benzylethylaniline, and therefore (as sodium salt) possessing the constitution



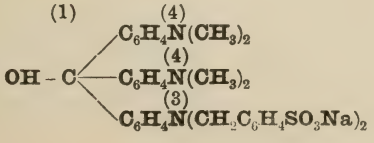
The form in which the colouring matter affixes itself to the fibre being probably



Another interesting dyestuff of this series is :—

Fast green [By], which is prepared by first condensing *m*-nitrobenzaldehyde with dimethylaniline; then reducing the nitro-group to the amido-group; and finally, after converting the amido-compound into its dibenzyl derivative, producing the disulphonic acid by sulphonation.

Its formula (sodium salt) is therefore

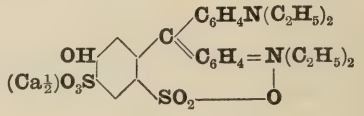


Patent blues.—In 1888 it was discovered by Hermann (E.P. 12,796[88], A.P. 412,613, 412,614, 412,615) that by the condensation of *m*-oxybenzaldehyde with symmetrically or unsymmetrically alkylated derivatives of aniline, leuco-compounds were produced, which could be converted into valuable greenish-blue dyestuffs on sulphonation and subsequent oxidation.

The same compounds can also be produced by starting with the corresponding *m*-nitro- or *m*-amido-derivative of benzaldehyde, and converting the nitro- or amido-group into hydroxyl by the usual methods, after condensation with the dialkylated aniline.

A typical member of the series is :—

Patent blue V, which, according to Erdmann (*Ann.*, 1897, ccxciv. 376), possesses the constitution



It is prepared by either of the following methods :—

(1) Condensation of 1 mol. *m*-nitrobenzaldehyde with 2 mols. of diethyl-aniline, with subsequent reduction.
Conversion of the *m*-amidotetraethyldiamidotriphenylmethane thus produced into the corresponding hydroxy-derivative by means of nitrous acid.
Sulphonation.
Conversion into the calcium (or magnesium) salt.
Oxidation.

(2) Condensation of *m*-oxybenzaldehyde with diethylaniline.
Sulphonation of the *m*-oxytetraethyldiamidotriphenylmethane thus formed.
Conversion into the calcium salt.
Oxidation.

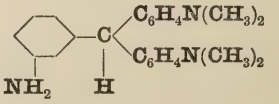
It is an important wool dye, particularly fast to light and alkali.

Other dyestuffs of this group are :—

Cyanol extra (Weinberg, 1891) or Acid blue 6G, prepared by using monoethyl-*o*-toluidine instead of diethylaniline in either of the above methods for preparing Patent blue V.

Patent blue A, prepared by using ethylbenzylaniline instead of diethylaniline.

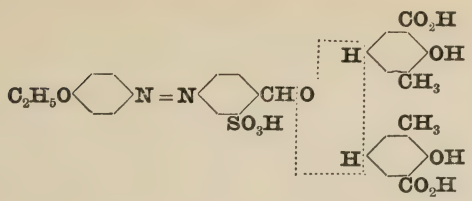
Azo green belongs both to the azo- and triphenylmethane dyestuffs, and is prepared by diazotising *m*-amidotetramethyldiamidotriphenylmethane



and combining the diazo-compound thus formed with salicylic acid. This leuco-base is finally oxidised.

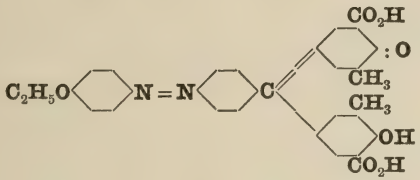
It is an important green mordant dyestuff.

Similar colouring matters having the azo-group in the para-position to the methane carbon atom are described by Green and Sen (*J.C.S.*, 1912, ci. 1113). Their mode of preparation and properties can be illustrated by referring to the compound formed by the condensation of phenetoleazobenzaldehydesulphonic acid with 2-hydroxy-*m*-toluic acid thus :—



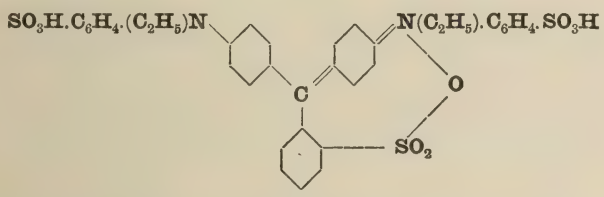
The substances, so far as their triphenylmethane structure is concerned, are "leuco" compounds, but are yellow dyestuffs by virtue of the azo-groups. Wool is therefore dyed orange-yellow, but the colour is oxidised and changed to black on the fibre by the action of potassium dichromate.

Oxidation of the "leuco"-compound by nitrosyl sulphate yields



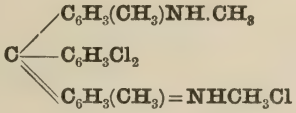
a dark-red compound possessing polygenetic properties.

Erioglaucine from benzaldehyde-*o*-sulphonic acid and ethylbenzylaniline-sulphonic acid is

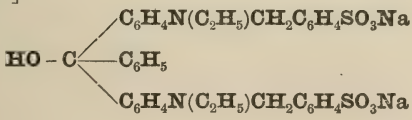


Other dyestuffs belonging to the Malachite green series are:—

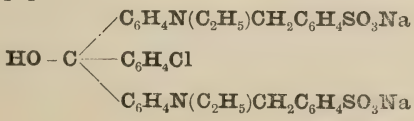
Glacier blue [J]



Guinea green B [A]



Neptune green SG [B]



(*b*) The Rosaniline Series.

In 1859 Prof. Verguin, of Lyons, made the discovery that a red dyestuff is formed when aniline is oxidised by tin chloride.

This product he named Fuchsin, and introduced its commercial manufacture in conjunction with the firm of Rénard Brothers, of Lyons.

The production of this important dyestuff led to the investigation of the action of other oxidising agents upon aniline, with the result that between 1859 and 1861 a large number of patents were taken out for the production of Fuchsin from aniline by the aid of various oxidising agents.

Chief amongst these are :—

Brooman	mercuric chloride.
Medlock, Nicholson, Girard and De Laire	arsenic acid.
Lauth, Laurent, Castelhaz, Coupier	nitrobenzene.

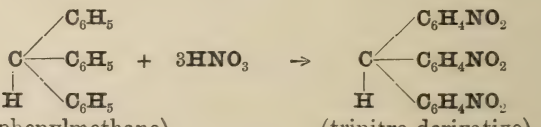
At the same time numerous chemists were engaged elucidating the constitution of Fuchsin (Magenta),[1] and also its method of formation, amongst these being A. W. Hofmann, O. and E. Fischer, Rosenstiehl, Döbner, Caro, Dale, Schorlemmer, and others.

The first important scientific research on the subject was that published by A. W. Hofmann in 1862 (*J. pr. Chem.*, 1862, lxxxvii. 226), who found this substance to be the salt of a base named by him rosaniline, which, on reduction, was converted into a base—leucaniline—characterised by forming colourless salts with acids.

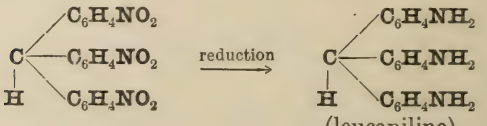
The successful elucidation of the constitution of Magenta is due to Otto and Emil Fischer (*Ber.*, 1880, xiii. 2204), who found that leucaniline is a primary triamine, which, on treatment with nitrous acid and boiling with absolute alcohol, is converted into triphenylmethane.

They further found that this hydrocarbon, on treatment with fuming nitric acid, is converted into a trinitro-derivative, which is reducible to leucaniline.

Thus :—

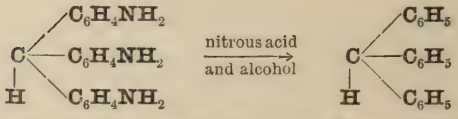


(triphenylmethane). (trinitro-derivative).



(leucaniline).

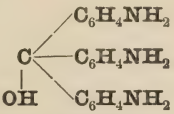
Also



[1] Magenta, the English name for this dyestuff, is used in this work.

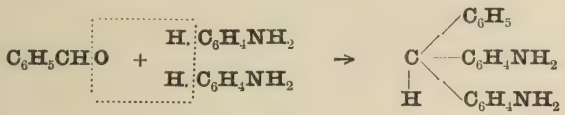
Consequently, leucaniline is a triamidotriphenylmethane, and the rosaniline base obtained from it, on oxidation, is a triamidotriphenylcarbinol

(leucaniline).

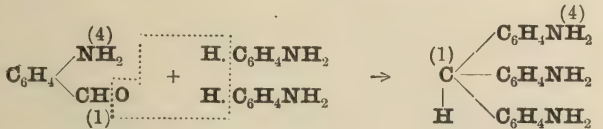

(rosaniline base).

The determination of the positions of the amido-groups in the three phenyl residues was carried out in the following way:—

When benzaldehyde is condensed with aniline in the presence of zinc chloride, diamidotriphenylmethane is produced



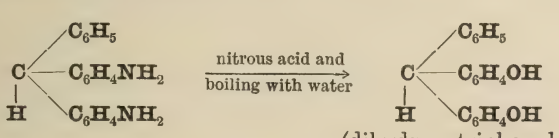
In the same way *p*-amidobenzaldehyde condenses with aniline to form a triamidotriphenylmethane (leucaniline), in which the position of one amido-group in reference to the methane carbon atom follows from the method of formation


(leucaniline).

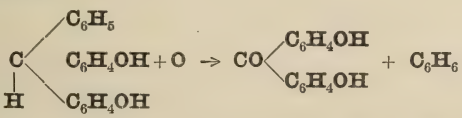
This amido-group is not either of those contained in the diamidotriphenylmethane mentioned above, and it is therefore only necessary to determine the positions of the two amido-groups in this substance in order to elucidate the constitution of leucaniline.

This was done in the following way:—

Diamidotriphenylmethane, on treatment with nitrous acid and boiling with water, is converted into dihydroxytriphenylmethane


(dihydroxytriphenylmethane)

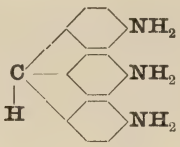
which, on fusing with caustic potash, is converted into dipara-dioxybenzophenone according to the equation



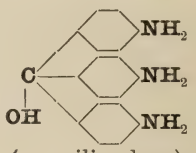
This substance had previously been prepared by Döbner (*Ber.*, 1879, xii. 1466), and in it the para-position of the two hydroxyl groups to the ketone group had been clearly established.

It therefore follows that the two amido-groups in the diamidotriphenylmethane are in the para-positions to the methane carbon atom, and hence that the three amido-groups contained in leucaniline are also in the para-position.

The formulæ, therefore, of leucaniline and the rosaniline base are



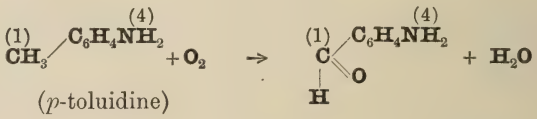
(leucaniline).



(rosaniline base).

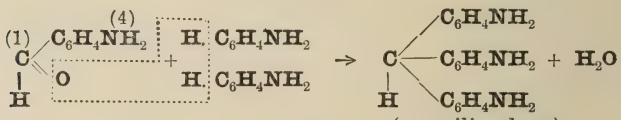
Shortly after the discovery of Magenta, Hofmann (*Ann.*, 1864, cxxxii. 296) showed that pure aniline did not give this dyestuff on oxidation, but that the presence of *p*-toluidine is necessary for its formation. This is explained on the assumption that the oxidising agent first acts on the methyl group of the *p*-toluidine, converting it into the aldehyde group, which then condenses with 2 mols. of aniline to form the base of the dyestuff. Thus :—

(1)



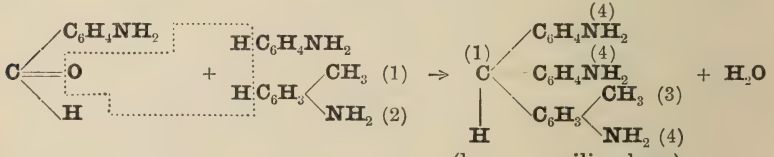
(*p*-toluidine)

(2)



(rosaniline base).

In actual practice an equimolecular mixture of aniline para- and ortho-toluidine are always used for the production of Magenta; consequently there is always present a second rosaniline formed according to the equation



(homorosaniline base).

The name homorosaniline was given in order to distinguish it from the other, which had been called para-rosaniline.

The latter name did not, however, refer in any way to the positions of the amido-groups, since at the time the name was given these positions were unknown.

Laws regulating the formation of dyestuffs of the Rosaniline series.—From the foregoing elucidation of the constitution of the rosaniline base, it is evident that in order that bases may be used in their preparation they must conform to certain well-defined conditions.

Thus, in the first place, one of the bases must contain a para-methyl group,

otherwise the requisite para-methane carbon atom cannot be furnished by oxidation.

Consequently neither ortho- nor meta-toluidine, either alone or in conjunction with aniline, can yield rosanilines on oxidation.

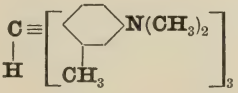
Again, it is evident that two molecules of the bases used must have their para-positions free, since it is at this point that union with the methane carbon atom takes place.

Thus para-toluidine when oxidised alone cannot yield rosaniline dyestuffs.

Rosenstiehl and Gerber divide the homologues of aniline into the three following classes:—

(1) The para-derivatives, which yield rosanilines when oxidised together with two molecules of the bases of class (2) or of aniline, but not by themselves.
(2) The ortho-derivatives, which yield rosanilines when oxidised with the bases of class (1), but not when oxidised alone or with aniline.
(3) The meta-derivatives, which under no circumstances yield rosanilines on oxidation.

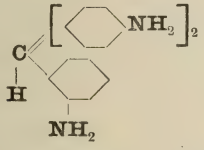
That rosanilines containing methyl groups in the meta-position to the amido-group are capable of existence has been demonstrated by E. Noelting, who has prepared a leuco-base of the formula



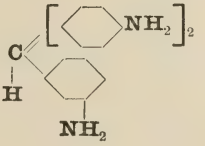
which gives blue rosaniline dyestuffs on oxidation. They are, however, prepared by indirect methods.

Noelting has also shown that it is possible to prepare rosaniline dyestuffs in which one of the amido-groups is in the ortho- or meta-positions to the methane carbon atom.

Thus the leuco-bases



and



yield rosaniline dyestuffs on oxidation.

If, however, less than two of the amido-groups are in the para-positions, then no rosaniline dyestuffs are formed from the leuco-bases on oxidation.

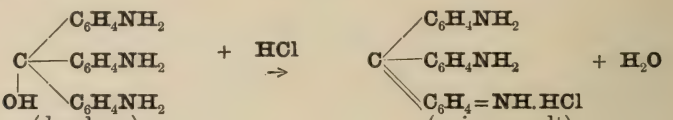
Formation of the dyestuff from the dye-base. Constitution of the Rosaniline dyes.—As already mentioned, the formation of the dyestuff from the dye-base is brought about by the action of dilute acids.

On treating the carbinol base with hydrochloric acid, one molecule of water is eliminated and a monochloride is formed; by the further action of hydrochloric acid a di- and a trichloride are formed, but these are produced without the elimination of water and must be considered as true salts caused by the passage of trivalent into pentavalent nitrogen.

Furthermore, the monochloride only is the true dyestuff, the further action of acid gradually destroying the colour.

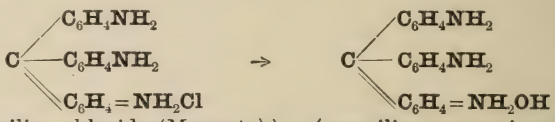
It is certain that, in the transformation of dye-base into the dye-salt, a change of constitution takes place, and that the triphenylmethane structure of the base passes into the quinone structure of the salt (*Nietzki*).

Thus :—



(dye-base). (quinone salt).

The existence of a quinone structure in dyestuffs of this series has received support by the discovery of v. Georgievics in the case of Magenta, and of Homolka in the case of New fuchsin of a second rosaniline base, which is coloured, and which in all probability is the ammonium base corresponding to the quinone salt given above.



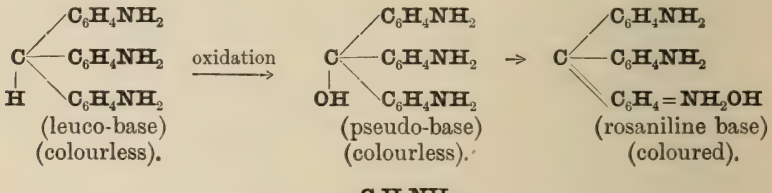
(rosaniline chloride (Magenta)). (rosaniline ammonium base).

The existence of this second rosaniline base was shown by electrical conductivity experiments (Hantzsch and G. Osswald, *Ber.*, 1900, xxxiii. 303), and it was found to be coloured and dissociated by potash, and therefore to behave as a true ammonium base.

The carbinol base, as already mentioned, is colourless, and is not dissociated to any appreciable extent.

The carbinol base of Magenta is therefore incapable of direct conversion into salts.

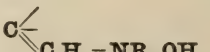
According to Hantzsch, it is a "pseudo-base," and, when transformed into the dye-salt, first undergoes conversion into the ammonium base, called by him the "rosaniline base."



(leuco-base) (colourless). (pseudo-base) (colourless). (rosaniline base) (coloured).

(rosaniline salt (dyestuff)).

According to Hantzsch and Osswald, the other coloured bases of this series behave in a similar way, the general formula of these ammonium bases being



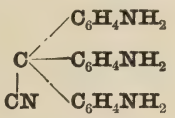
where R = hydrogen or any monovalent hydrocarbon radical.

Another view concerning the constitution of rosaniline chloride is that advanced by Rosenstiehl, according to which rosaniline is a tertiary alcohol and its chloride the chlorine ester thereof.

(rosaniline base). (rosaniline chloride).

Apart, however, from any question concerning the salt-like character of rosaniline chloride, this view is rendered improbable by the very different properties exhibited by a cyanide of this formula prepared by E. Fischer and W. L. Jennings (*Ber.*, 1893, xxvi. 2221).

This substance, which undoubtedly has the constitution



is colourless, insoluble in water, and unacted upon by cold alkalies.

It is interesting to note that Otto Fischer has found that *p*-amidobenzyl alcohol

$$OH.CH_2.C_6H_4.NH_2$$

behaves very similarly to rosaniline on conversion into its hydrochloride.

Thus when treated with hydrochloric acid the normal colourless hydrochloride is formed

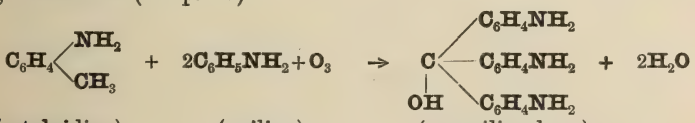
$$OH.CH_2.C_6H_4NH_2.HCl$$

If this is heated at 100° C., water is eliminated, and a coloured chloride is produced, which possesses the property of dyeing silk yellow from an alcoholic solution.

On dissolving in water the coloured chloride again becomes colourless, owing to its reconversion into the normal hydrochloride.

Methods of formation.—The following methods are in use for the preparation of members of the Rosaniline series.

(1) By *the oxidation of p-amines* together with such bases as are capable of yielding rosanilines (see p. 87).

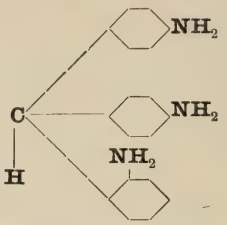


(*p*-toluidine). (aniline). (rosaniline base).

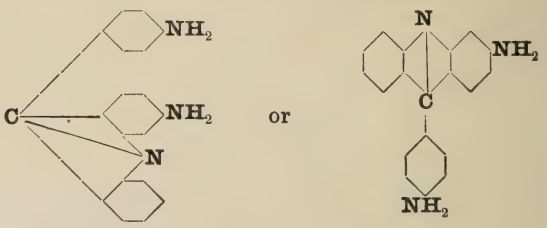
Arsenic acid and nitrobenzene are the oxidising agents most usually employed. The latter has now, however, practically superseded the former, since, in consequence of the impossibility of freeing the finished dyestuff from the last traces of arsenic, the product formed by the former agent frequently possessed poisonous properties.

The process is more fully described on p. 272.

In the production of Magenta, the yellow dyestuff Chrysaniline occurs as a bye-product; this is evidently formed by the occurrence of a partially ortho-condensation, giving rise to the substance



which, on further oxidation, is converted into Chrysaniline.



Chrysaniline is, therefore, a diamidophenylacridine.

(2) The *New magenta process* [M].—Formaldehyde is condensed with *o*-toluidine to form anhydroformaldehyde-*o*-toluidine

$$CH_2O + H_2NC_6H_4CH_3 \rightarrow CH_2 : NC_6H_4CH_3 + H_2O$$

(formaldehyde). (toluidine). (anhydroformaldehyde-*o*-toluidine).

On heating this substance with *o*-toluidine and *o*-toluidine hydrochloride it is converted by molecular rearrangement into diamidotri-*o*-tolylmethane

$$CH_2 : NC_6H_4CH_3 + C_6H_4CH_3NH_2 \rightarrow CH_2 = (C_6H_3CH_3NH_2)_2$$

This latter substance is readily converted into New magenta on heating with *o*-toluidine hydrochloride in the presence of an oxidising agent; and the process is capable of wide application, since many bases other than toluidine can be used, giving rise to other dyestuffs of this series.

(3) *Phosgene process* [B].—When phosgene gas, $COCl_2$, is allowed to react on dimethylaniline in the presence of zinc chloride, tetramethyldiamidobenzophenone is formed

$$COCl_2 + 2HC_6H_4.N(CH_3)_2 \rightarrow CO(C_6H_4.N(CH_3)_2)_2 + 2HCl$$

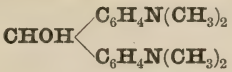
(phosgene). (dimethylaniline). (tetramethyldiamidobenzophenone).

This ketone, on treatment with phosphorus oxychloride, is converted into the dichloride

$$CCl_2(C_6H_4N(CH_3)_2)_2$$

which condenses with many bases, forming derivatives of rosaniline.

(4) By condensing tetra-alkylated diamidobenzhydrol



prepared by the oxidation of tetramethyldiamidotriphenylmethane, with bases and phenols [By].

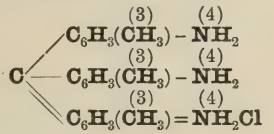
General description of the dyestuffs of the Rosaniline series.—The Rosaniline dyestuffs, except in the form of their sulphonic acid (to be described later), are basic dyestuffs, dyeing wool and silk direct, but requiring the aid of tannin to affix themselves on the cotton fibre.

Magenta (Fuchsin, etc.) occurs commercially as the chloride (more rarely as the acetate) of para- and homorosaniline.

The mixture of bases, aniline, *o*- and *p*-toluidine, used in its formation is known technically as "Aniline oil for red."

The purest form of Magenta is known as Diamond magenta, and finds application rather as a basis for the preparation of other dyestuffs of the series than for use as a dyestuff itself.

New magenta [M] is tritolylrosaniline chloride



and is produced from *o*-toluidine by the New magenta process (see above).

If the hydrogens of the amido-group in Magenta are replaced by alkyl groups, violet dyestuffs are formed, which approximate more closely to the blue or red, according as the number of alkyl groups is greater or less.

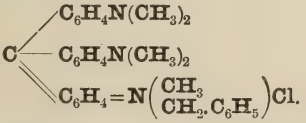
The *Methyl violets* are a number of dyestuffs belonging to this series in which the letters R, 2R, 3R, B, 2B, 3B, etc., are affixed in order to denote the red or blue shade of the dyestuff.

The most usual method adopted in their preparation is to oxidise dimethylaniline with cupric chloride in the presence of phenol. The course of this reaction is as follows:—

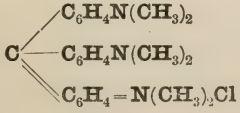
A methyl group of the dimethylaniline is oxidised to formaldehyde, which condenses with the resulting methylaniline and two molecules of the unaltered dimethylaniline to form pentamethylrosaniline.

The bluest methyl violet, *Methyl violet* (6B), that can be prepared by this method is made by treating pentamethylrosaniline with benzyl chloride, thus converting it into the benzyl derivative.

It therefore has the constitution

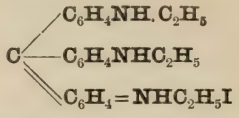


Hexamethylrosaniline chloride is known as *Crystal violet*



and is prepared by the phosgene method.

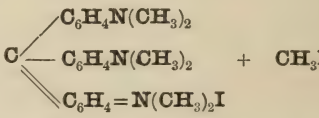
Hofmann's violet was the first violet dyestuff of this series prepared, and is now merely of historical interest. It is triethylrosaniline iodide



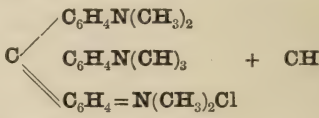
By the addition of alkyl iodides and chlorides to the violet rosaniline dyestuffs, there are formed a series of green dyestuffs, which are addition products of the alkylated rosaniline salt and the alkyl halogen compound.

They have for the most part been replaced by other green dyestuffs, since, being quaternary salts, they are split up at a comparatively low temperature into the alkyl halogen compound and the violet dyestuff from which they were derived.

Iodine green is prepared by treating methyl violet with methyl iodide. Its formula is



At one time this dyestuff was very largely used, but was soon replaced by the corresponding *Methyl green*

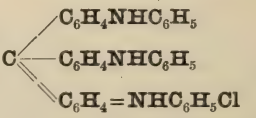


prepared in a similar way from methyl violet and methyl chloride.

This dyestuff is still, to some extent, used for the dyeing of cotton on a tannin mordant, for which purpose it is better suited than Malachite green, which has, however, completely replaced it as a wool dye.

Phenyl and tolyl derivatives of rosaniline.—On heating rosaniline with aniline or toluidine in the presence of acetic or benzoic acid, there are formed, in the first instance, violet dyestuffs which consist of mono- and diphenyl (or tolyl) rosanilines; these, by the further action of aniline or toluidine, pass into the blue dyestuffs known as the *Rosaniline blues.*

The compound formed from aniline and pararosaniline therefore has the formula (hydrochloride)



and was discovered by Girard and de Laire in 1861, the first product, which was insufficiently phenylated, and therefore of a violet shade, being sold under the name of Lyons blue.

The aniline used in the product of this Rosaniline blue must be quite pure; technically it is known as "Aniline oil for blue."

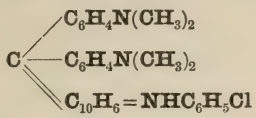
The introduction of three phenyl groups into the pararosaniline molecule, one attached to each nitrogen of the three amido-groups, represents the extent to which it can be phenylated. It is apparently impossible to introduce two phenyl

groups on to the same nitrogen atom. The dyestuffs prepared in this way are insoluble in water, but readily become soluble on treatment with sulphuric acid (see *Alkali blue*, etc.); they are therefore of little importance by themselves, but serve for the production of their important sulphonic acids.

Diphenylamine blue, which is identical with triphenylpararosaniline blue, was prepared in 1866 by Girard and de Laire, by heating diphenylamine with oxalic acid, and for a considerable time competed successfully with Rosaniline blue.

A number of important dyestuffs of this group are manufactured by the Badische Anilin und Soda Fabrik from the tetraalkyldiamidobenzophenones.

Thus *Victoria blue* B is prepared by condensing tetramethyldiamidobenzophenone with phenyl-α-naphthylamine, and therefore has the constitution



Other dyestuffs prepared from this ketone are :—

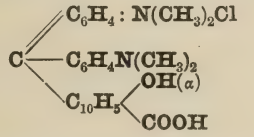
Victoria blue 4R, with methylphenyl-α-naphthylamine, and
Victoria blue R, with ethyl-α-naphthylamine.

Night blue is prepared from tetraethyldiamidobenzophenone and *p*-tolyl-α-naphthylamine. It possesses the curious property of forming insoluble compounds with certain dyestuffs—such as, for example, Picric acid and Naphthol yellow S—which causes it to be used in the quantitative estimation of these compounds (see p. 342).

Another interesting series of colouring matters which belong to the triphenylmethane series are the Chrome colours of Fr. Bayer & Co. They are made by condensing tetraalkyldiamidobenzhydroles with certain aromatic acids — such as benzoic acid, salicylic acid, oxynaphthoic acid, etc.—in the presence of sulphuric acid, and subsequently oxidising the product.

An example is :—

Chrome blue, made by condensing tetramethyldiamidobenzhydrol with α-oxynaphthoic acid, followed by oxidation. Its constitution is



It is a mordant dyestuff, forming green lakes with chromium salts.

Other dyestuffs of this nature, prepared in the same way from tetramethyldiamidobenzhydrol, are :—

Chrome violet with salicylic acid, and
Chrome green with benzoic acid.

Sulphonic acids of the Rosaniline dyestuffs.—It was discovered by Nicholson, in 1862, that the insoluble triphenylrosaniline chloride (Rosaniline blue), when treated with concentrated sulphuric acid, was converted into a sulphonic acid, the sodium salt of which was soluble in water and could be used as an acid dyestuff for the dyeing of wool.

This important discovery led to the preparation of a large number of other acid dyestuffs, by the sulphonation of members of the Rosaniline series, which

are far better adapted for the dyeing of wool than the basic dyestuffs from which they are derived. The Nicholson method of sulphonating dyestuffs is of great practical importance, and can be applied to most classes of dyes.

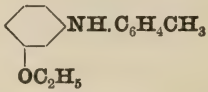
The sulphonic acid groups can be introduced either by (*a*) sulphonating the dyestuff, (*b*) sulphonating the leuco-base, or (*c*) using substances already containing sulphonic acid groups in the preparation of the dyestuff.

Acid magenta (Fuchsin S) is usually the acid sodium salt of a mixture of the mono- and disulphonic acid obtained by the sulphonation of Magenta.

Acid violets.—A number of dyestuffs of this name, distinguished by the addition of various letters, are met with in commerce.

They are for the most part sodium salts of the various sulphonic acids, obtained by the sulphonation of the Methyl violets (see p. 91).

Acid violet 6 BN [B] is a phosgene colour, and is prepared by sulphonating the condensation product of tetramethyldiamidobenzophenone with *m*-ethoxyphenyl-*p*-tolylamine,



The following dyestuffs are formed by the sulphonation of Rosaniline blue :—

Nicholson blue or *Alkali blue* is the sodium salt of the monosulphonic acid of Rosaniline blue.

It is largely used as an acid wool dye. Its method of application is, however, peculiar.

The wool is first boiled in a solution of the dyestuff made alkaline with borax, when the dye is affixed to it in the form of an almost colourless derivative.

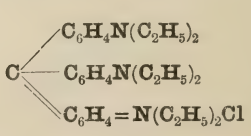
The colour is developed on treatment with dilute sulphuric acid.

Water blue, Cotton blue, Navy blue, Soluble blue, etc., are names given to a number of blue acid dyestuffs which are for the most part mixtures of the ammonium (or sodium salts) of the di- and trisulphonic acids of Rosaniline blue.

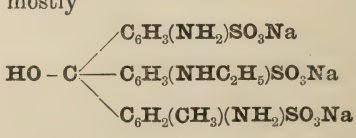
It is worthy of remark that these sulphonic acids are to some extent capable of forming lakes with tannin, and hence can be used as cotton dyes on a tannin mordant.

Other dyestuffs of the Rosaniline series not mentioned above are :—

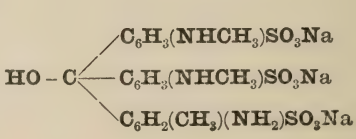
Ethyl violet [B]



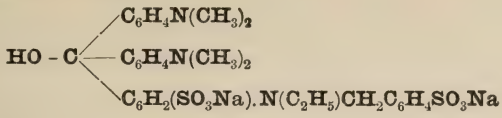
Red violet 5RS [B], mostly



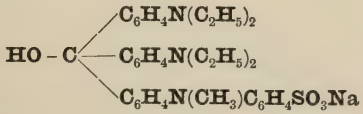
Red violet 4RS [B]



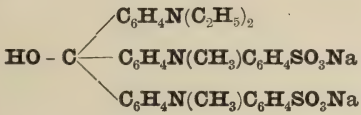
Fast acid violet 10B [By]



Alkali violet [B]



Acid violet 7B [B]

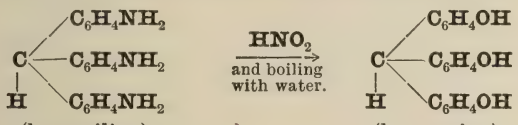


(*c*) The Rosolic Acid Dyestuffs.

Rosolic acid belongs to the oldest of the artificial dyestuffs, having been prepared by Runge in 1834.

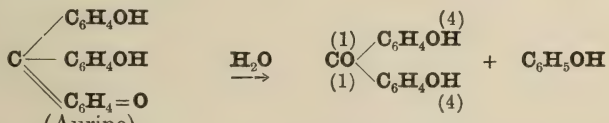
In 1861 Kolbe and Schmidt, and Jul. Persoz independently, discovered that it could be prepared by heating together phenol and oxalic acid with sulphuric acid.

The constitution of Aurine follows from the fact that its leuco-compound can be prepared from leucaniline by treating it with nitrous acid and boiling with water



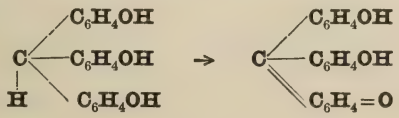
(leucaniline). (leucaurine).

And also from the fact that on heating with water at 220° it is broken up into phenol and *p*-dioxybenzophenone.

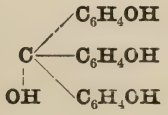


(Aurine).

The dyestuff rosolic acid (*Aurine*) is directly formed by the oxidation of its leuco-compound

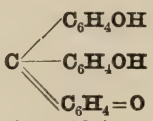


The intermediate carbinol



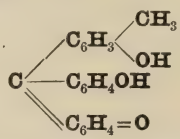
appears to be incapable of existence, although Herzig has succeeded in preparing its triacetyl derivative.

Since Aurine can be prepared from rosaniline, it is obvious that two dyestuffs exist corresponding to para- and homorosaniline respectively. They are called



(pararosolic acid (Paraaurine)),

derived from pararosaniline, and

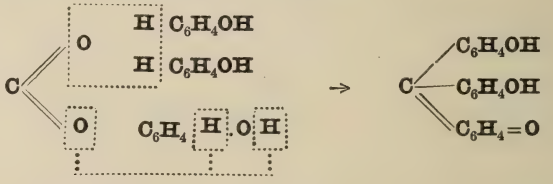


(homorosolic acid (Homoaurine)),

derived from homorosaniline.

As already mentioned, Aurine is prepared by the action of sulphuric acid on a mixture of phenol and oxalic acid.

This reaction is explained on the assumption that the carbon dioxide (from sulphuric and oxalic acids) supplies the necessary methane carbon atom, and that the condensation ensues according to the equation



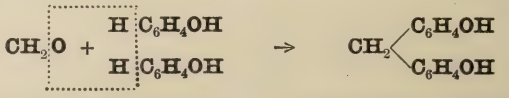
Aurine is no longer used as a dyestuff in the strict sense of the term. Owing, however, to its sensitiveness to alkalies it is frequently used as an indicator in alkalimetry.

Paeonine (Red corallin) is prepared by heating crude Aurine (Yellow corallin) with ammonia under pressure.

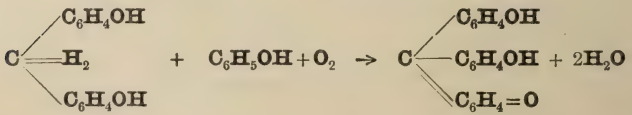
It is used for producing shades varying in colour between Magenta and Cochineal, and probably consists in part of a rosolic acid salt of *p*-rosaniline.

Lately compounds belonging to this group have been prepared by a process analogous to the New magenta process described on p. 90.

Thus Aurine can be prepared in the following way :—



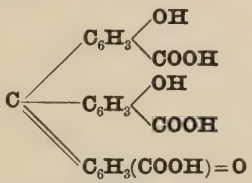
(formaldehyde). (phenol). (dioxydiphenylmethane).



(Aurine).

By replacing the phenol by other substances—such as resorcinol, pyrogallol, etc.—dyestuffs analogous to Aurine have been prepared.

Thus *Chrome violet* [R. Geigy of Basle] is

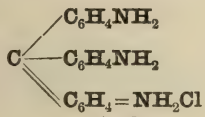


and is prepared from formaldehyde and salicylic acid.

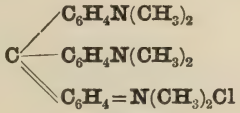
The Influence of Groups and Constitution upon the Colour of Compounds of the Triphenylmethane Series.

Probably no other series of dyestuffs illustrates to such a marked extent the influence of the auxochrome groups, NH_2 and OH, as the compounds of the triphenylmethane series.

Thus Magenta is red, hexamethylmagenta (Crystal violet) is violet



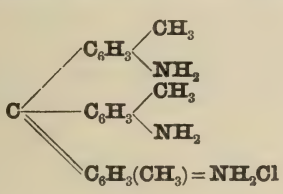
(red),



(violet),

and the various brands of the Methyl violets are intermediate in colour between red and violet, according as more or less of the hydrogens of the amido-groups are replaced by methyl.

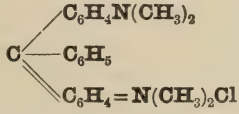
If, however, the methyl groups enter into the benzene nuclei, the colour of the dyestuff is not appreciably affected. Thus New magenta



is red.

By the elimination of one of the amido-groups in Magenta, green dyestuffs are produced.

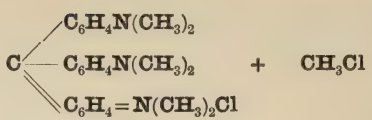
For example, Malachite green



The same change in colour takes place if, instead of the amido-group being eliminated, its basic character is destroyed by the entrance of acetyl groups.

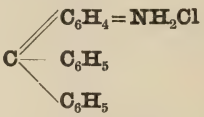
Green dyestuffs of the triphenylmethane series are also produced by the addition of methyl chloride to the violet hexamethylrosaniline chloride.

Thus Methyl green is



If two amido-groups in rosaniline are lacking, the colour of the compound is not quite destroyed.

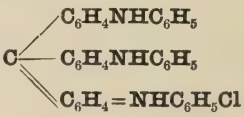
Thus *p*-monoamidotriphenylmethane chloride



is orange yellow, and will affix itself to tannined cotton.

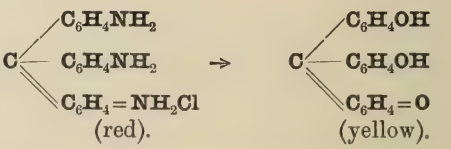
By the entrance of phenyl groups in place of the hydrogens of the amido-groups in rosaniline, the colour gradually passes from red to blue.

Thus the highest phenylated rosaniline—triphenylrosaniline chloride—



is blue.

The replacement of the amido-groups by hydroxyl groups gives rise to the Aurines, which are yellow.



The entrance of sulphonic acid groups into the molecule of rosaniline and its derivatives apparently does not appreciably affect the tone of the colour, although its colour-strength is thereby considerably diminished.

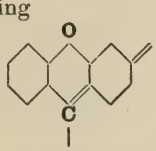
This is, however, counterbalanced by the increased solubility of the dyestuff in water.

CHAPTER XV.

PYRONINE DYESTUFFS.

The dyestuffs of this group contain as chromophore the para-quinone ring

and as chromogen the pyronine ring



They can be divided into—

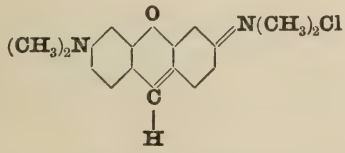
(1) Diphenylmethane derivatives, comprising the Pyronines.

(2) Triphenylmethane derivatives, comprising the Phthaleïns.

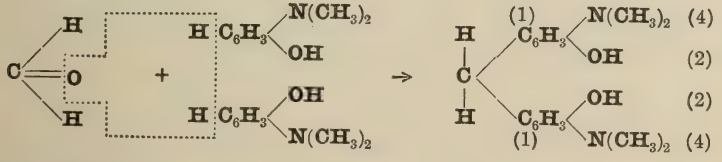
(1) The Pyronines.

Dyestuffs of this class are produced by the condensation of dialkyl *m*-amidophenol with aldehydes and acids of the aliphatic series.

Pyronine G [L]



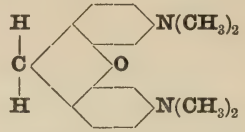
is prepared (E.P. 8673[89], 13,217[89], 18,606[91], A.P. 445,684) by the condensation of formaldehyde with dimethyl-*m*-amidophenol to form tetramethyldiamidodioxydiphenylmethane



(formaldehyde). (dimethyl-*m*-amidophenol). (tetramethyldiamidodioxydiphenylmethane).

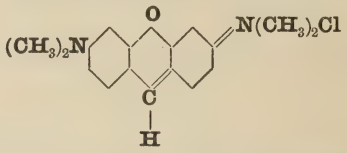
In this compound the hydroxyl groups are in the ortho-position to the methane carbon atom, and therefore, as will be found to be always the case in

dyestuffs of the Pyronine and Phthaleïn series, readily split off water to form the internal anhydride

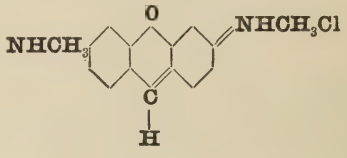


(tetramethyldiamidodiphenylmethane oxide),

which, on oxidation and conversion into the salt, forms the dyestuff

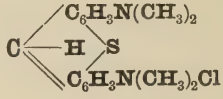


On oxidation with potassium permanganate, Pyronine G is converted into *Acridine red* (E.P. 1231[92])



The Pyronines are more or less yellowish-red, fluorescent, basic dyestuffs, which are chiefly used in the dyeing of tannined cotton.

According to D.P. 65,739, dyestuffs of this class containing sulphur in the place of oxygen can be prepared by the action of S_2O_3 on alkylated diamidodiphenylmethanes dissolved in concentrated H_2SO_4. Their constitution would be represented by the formula

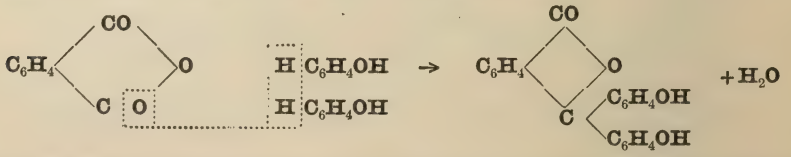


(2) The Phthaleïns.

These dyestuffs are produced by the condensation of phthalic anhydride with phenol or amidophenols, the condensation being usually brought about in the presence of some dehydrating agent, such as zinc chloride, sulphuric acid, etc.

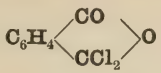
The most typical instance of the formation of a phthaleïn is shown in the formation of phenolphthaleïn from phthalic anhydride and phenol (*Baeyer*, 1871).

These substances unite in accordance with the equation



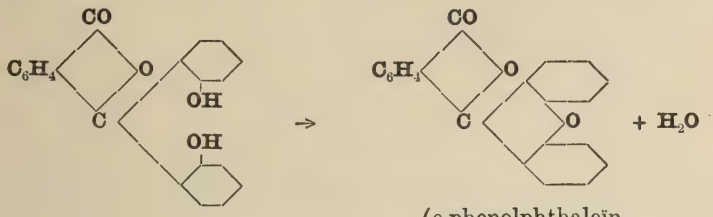
the hydrogens in the para-positions of the two phenol molecules reacting with the oxygen of one of the carbonyl groups.

The correctness of this formula is shown by the fact that phthalyl chloride



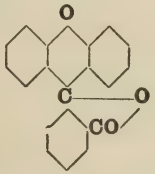
also combines with phenol to form phenolphthaleïn.

In the formation of phenolphthaleïn, however, a certain amount of the product consists of *o*-phenolphthaleïn anhydride, which has obviously been formed by the combination of the phenol molecules in the ortho-position, with subsequent elimination of water



(*o*-phenolphthaleïn anhydride),

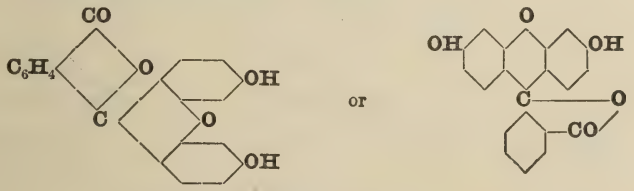
or written as a pyronine derivative



It is this substance which may be considered as the chromogen of the phthaleïn dyestuffs, since by the entrance of auxochrome groups into its molecule, bases or acids are formed which, when converted into their salts, yield the Rhodamines and Eosines.

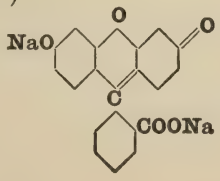
Just as in the Triphenylmethane series and in the Pyronine series already dealt with, the transformation of bases or acids of these dyestuffs into their salts is assumed to be accompanied by a change of constitution from the phthaleïn form into the quinone structure (see p. 109).

Thus

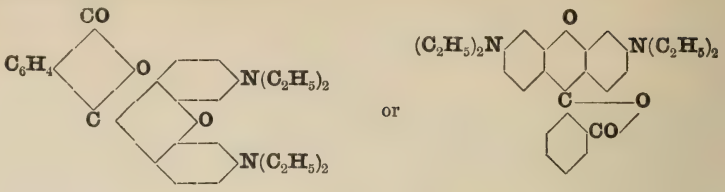


(*Fluoresceïn (acid)*),

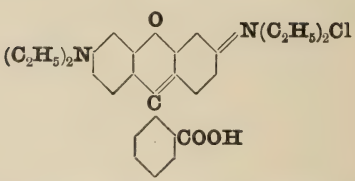
gives the sodium salt (Uranine)



and Rhodamine B [B] (base)

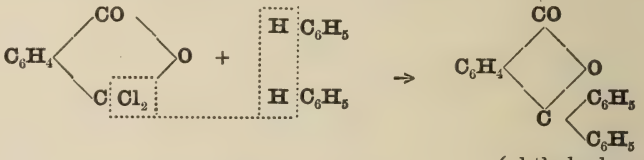


gives the chloride



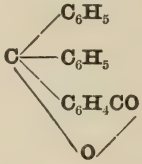
The relationship that exists between the members of the phthaleïn series and triphenylmethane is shown by the following facts:—

Phthalyl chloride condenses with benzene in the presence of aluminium chloride (*Friedel* and *Crafts*) to form phthalophenone

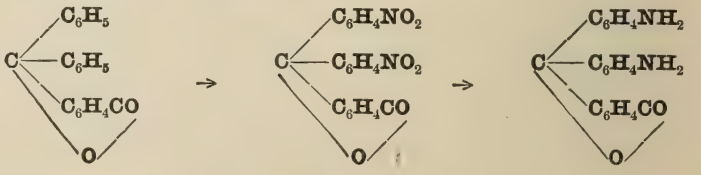


(phthalophenone),

or if written as a triphenylmethane derivative

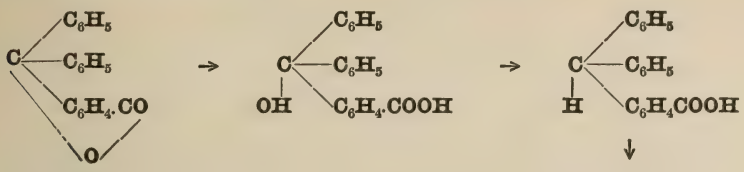


This substance can be either (1) converted into phenolphthaleïn by nitration, reduction, diazotisation, and boiling with water



(phenolphthaleïn),

or (2) converted into triphenylmethane by treatment with alcoholic KOH, reduction, and dry distillation

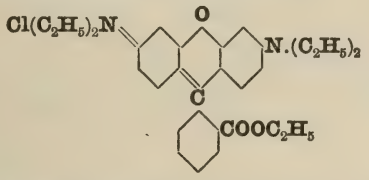


The Rhodamines.

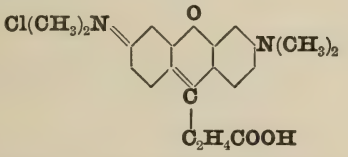
These dyestuffs are phthaleïns, derived from the combination of dialkyl-*m*-amidophenol with phthalic anhydride. The Rhodamine B already mentioned is typical of their constitution.

They are basic dyestuffs, dyeing wool and silk direct a bluish-red showing strong fluorescence. On tannined cotton this fluorescence is lost, and the colour appears as a dull shade of lilac, but it is retained if the cotton is mordanted with Turkey-red oil and alumina.

By etherification (replacement of the hydrogen of the carboxyl group by C_2H_5), Rhodamine B passes into *Rhodamine* 3B [B]



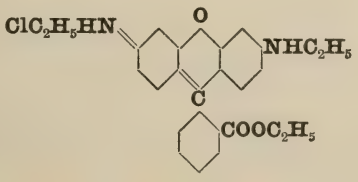
An interesting dyestuff, belonging to this group, is prepared by condensing succinic anhydride with dimethyl-*m*-amidophenol. It is known as *Rhodamine* S [B], and has the constitution (chloride)



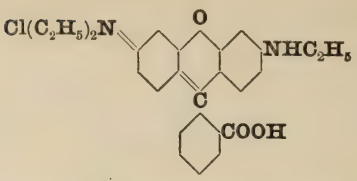
It is a substantive cotton dye, dyeing unmordanted cotton a fairly fast shade of pink.

Other dyestuffs belonging to this group are :—

Rhodamine 6G [B]

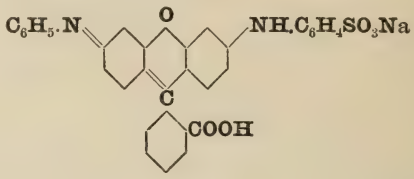


Rhodamine G [B]

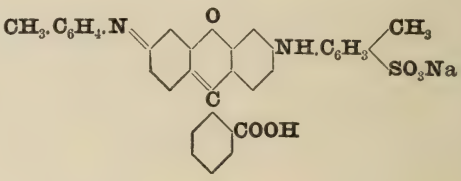


and the following sulphonic acids (made by the sulphonation of the condensation product) :—

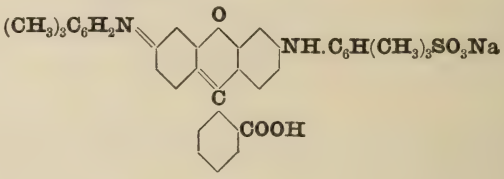
Fast acid violet B [M]—Violamine B



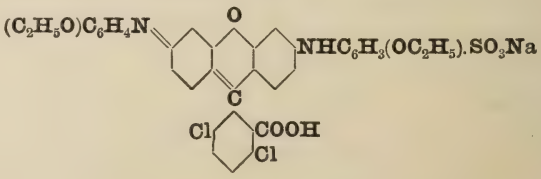
Fast acid violet A, 2R [M]—Violamine R



Acid rosamine A [M]—Violamine G



and Fast acid blue R [M]—Violamine 3B

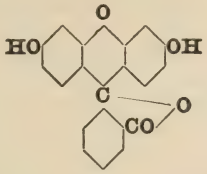


The Eosines.

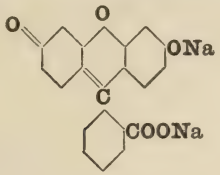
These dyestuffs are prepared by the condensation of phthalic anhydride with di- and trihydric phenols.

Most of the members of this group are, however, derived from Fluoresceïn, which is prepared by the condensation of phthalic anhydride and resorcinol in the presence of zinc chloride.

The free phenol has, therefore, the constitution



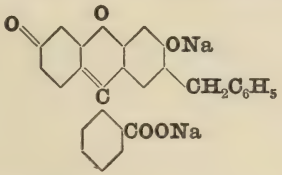
whilst the sodium salt, which is found in commerce under the name of *Uranine*, has the constitution



It is an acid dyestuff, forming solutions in water which exhibit a remarkable green fluorescence. It is, however, of little importance.

Another dyestuff of this group is *Chrysoline* [Mo], which was prepared in 1877 by Reverdin by the interaction of resorcinol, phthalic anhydride, and benzyl chloride in the presence of sulphuric acid.

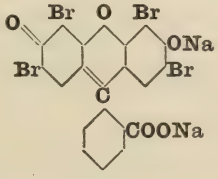
Its sodium salt is best represented by the constitution



It is chiefly important as a silk dye.

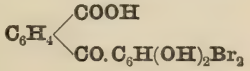
In 1874 Caro found that Fluoresceïn was capable of absorbing bromine, and was thereby converted into a red dyestuff, to which he gave the name *Eosine*.

Eosine A [B] is a tetrabromofluoresceïn containing two bromine atoms on each of the benzene rings of the two resorcinol residues, and as sodium salt has the constitution



These positions have been determined in the following manner:—

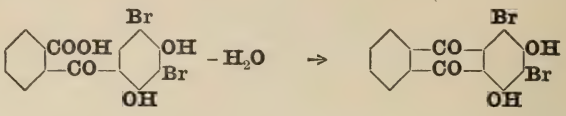
By boiling Eosine with caustic soda a dibromodihydroxybenzoylbenzoic acid



is produced (*A. Baeyer*).

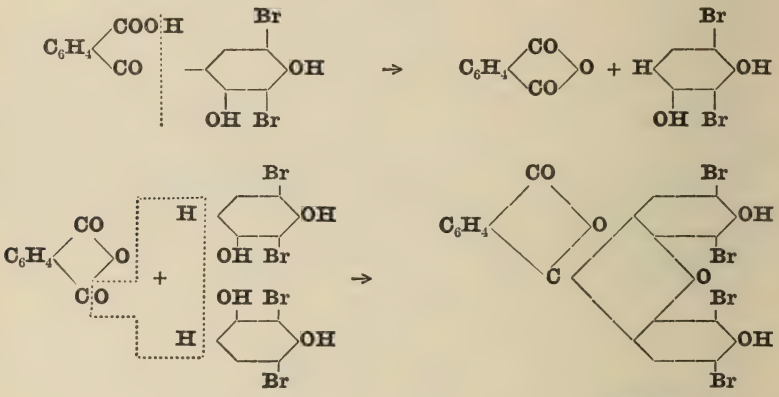
In this substance the bromine atoms must necessarily occupy the same positions as they do in one of the benzene rings of Eosine.

Its constitution has been determined by G. Heller, who succeeded, by the aid of fuming sulphuric acid, in converting it into an already known dibromoxanthopurpurine



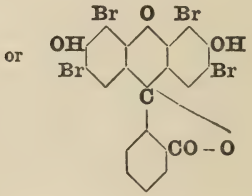
Finally, R. Meyer, by heating it to a temperature above its melting-point, transformed it into Eosine and phthalic acid.

This reaction, which evidently takes place in accordance with the following equations :—



(Eosine),

or

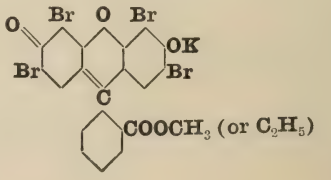


definitely establishes the positions of the bromine atoms in Eosine.

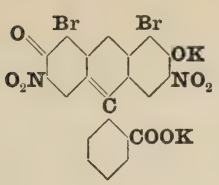
Eosine is used more especially as a silk dye, upon which the shades produced are yellowish-red showing a marked fluorescence.

The following list gives the various dyestuffs of this group which are produced, some by the entrance of other halogens into Fluoresceïn, others by the conversion of Eosine into its derivatives.

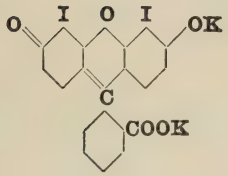
Spirit eosine [TM] and *Eosine* S [B] are the methyl and ethyl esters of Eosine respectively, constituted according to the formula



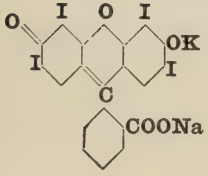
Eosine BN [B]



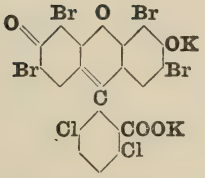
Erythrosine G [B]



Erythrosine [B]

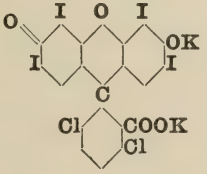


Phloxine P [B]

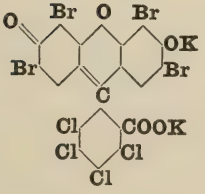


Spirit cyanosine [M] is the methyl ether of Phloxine P.

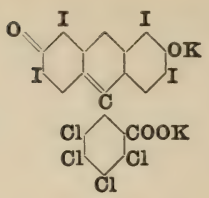
Rose Bengal [B]



Phloxine [M]



and Rose Bengal 3B [M]



The above compounds, which contain chlorine in the phthalic residue, are derived from dichloro- and tetrachlorophthalic acid respectively.

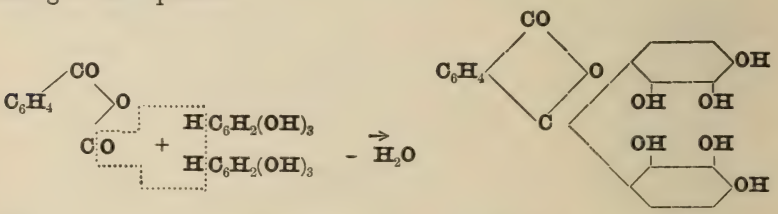
Galleïne and Cœruleïne.

These are two dyestuffs which, owing to their method of formation, are classed among the phthaleïns, but which in their application are more akin to the next group of dyestuffs, that of the Alizarine series.

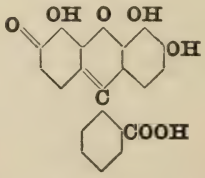
They are mordant dyes, forming, in the case of Galleïne, blue; and, in the case of Cœruleïne, green lakes with chromium salts.

Galleïne [B] is formed by heating phthalic anhydride with gallic acid at 200°.

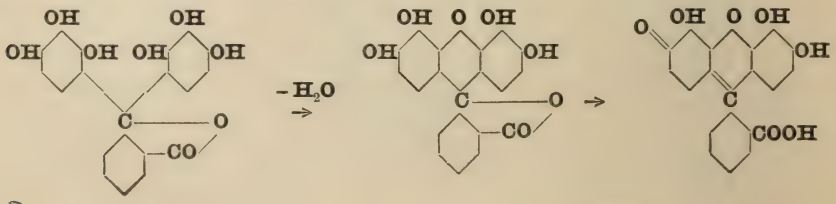
Since at this temperature gallic acid breaks up into pyrogallic acid and carbon dioxide, it is evidently the former which condenses with phthalic anhydride, according to the equation



The empirical formula of Galleïne is, however, $C_{20}H_{12}O_7$, and its constitution, according to Orndorff and Brewer (*Amer. Chem. J.*, 1901, 97; also *J.C.S.*, 1901, abs. i., 724), is

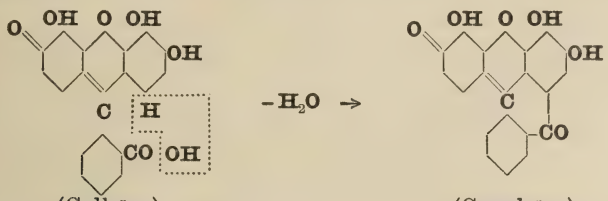


This formula is derived from the above by the elimination of water and conversion into a quinone structure



Cœruleïne [B] is prepared by heating Galleïne with concentrated sulphuric acid at 200°.

According to Orndorff and Brewer (*loc. cit.*) its constitution is represented by the formula

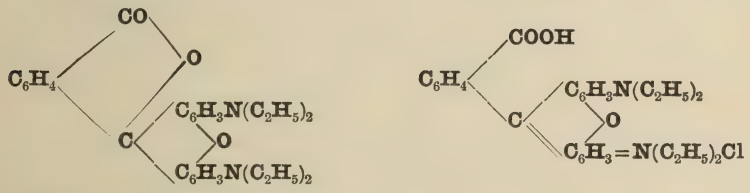


(Galleïne). (Cœruleïne).

Like Galleïne it is insoluble in water, and is usually fixed on the fibre by the aid of its chromium lake (*Green*). It is generally found in commerce in the form of a 10 per cent. paste.

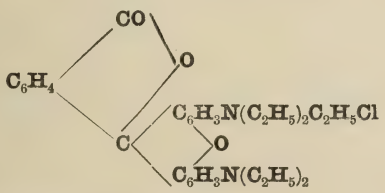
In the form of its soluble bisulphite compound it is known as *Cœruleïne* S.

The Constitution of the Pyronines.—The experimental data upon which it has been assumed that the transformation of the colourless Rhodamine base into its intensely coloured salt is accompanied by a change of constitution from the lactone to the quinone form

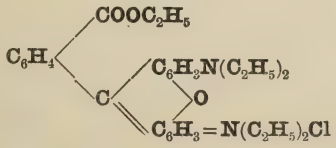


are as follows :—

A Rhodamine of the above constitution gives an ethereal salt when treated with an etherifying agent, such as alcohol and hydrochloric acid. This ethereal salt is readily hydrolysed to the corresponding acid, and therefore cannot be a quaternary ammonium salt of the formula



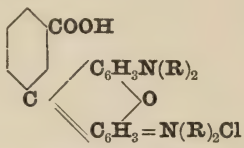
but must have the constitution represented by



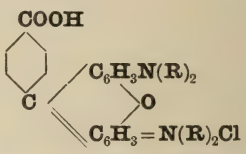
Strong support has been given to this view by the work of Noelting and Paira, who condensed nitrobenzaldehyde with *m*-amidophenol, effected the closing

of the pyrone ring by eliminating water from the hydroxyl groups, and finally displaced the nitro-group by carboxyl.

The dyestuffs thus formed, which must, from their mode of preparation, contain a carboxyl group, are very similar in character to the Rhodamines; they are represented by the formulæ

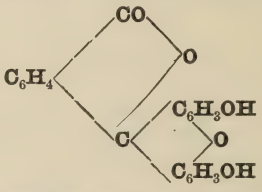


and

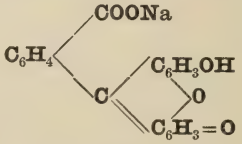


(From *m*-nitrobenzaldehyde.) (From *p*-nitrobenzaldehyde.)

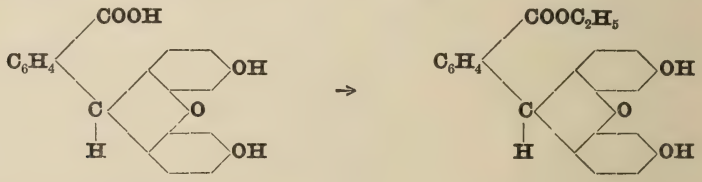
By analogy, Fluoresceïn should have the constitution



whilst its intensely coloured sodium salt should have the constitution

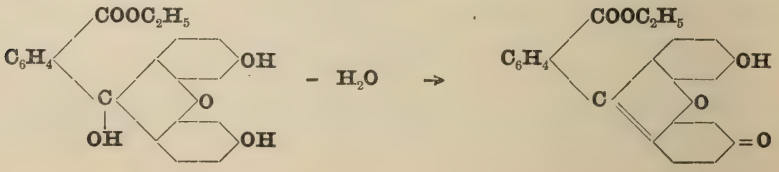


This question has been thoroughly investigated by the researches of O. Fischer, Hepp, Nietzki, and Schroeter, who find that this substance may exist both in the lactone and quinone forms, the former being the more stable of the two. For example, Nietzki and Schroeter found that on treating Fluorescin (prepared by the reduction of Fluoresceïn) with alcohol and hydrochloric acid it was transformed into an ethyl salt



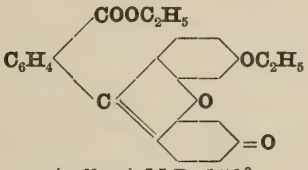
(Fluorescin),

which, on oxidising and eliminating water, was converted into a corresponding ethyl salt, which must have a quinone structure



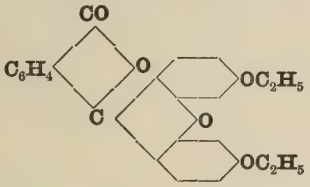
By the bromination of this quinone ester they obtained an ethyl salt of Eosine, from which it follows that the Eosines also possess a quinone structure.

By the further etherification of the quinone monoethyl salt of Fluoresceïn mentioned above, they obtained a diethyl salt of the constitution



(yellow) M.P. 159°,

which is isomeric, and not identical, with the diethyl salt of the constitution

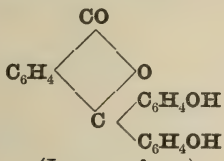


(colourless) M.P. 181–182°.

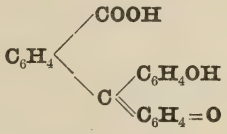
(Nietzki and Schroeter, *Ber.*, xxviii. 47.)

By the alkylation of Fluoresceïn salts, the production of the coloured quinone diethyl salt is always accompanied by that of the colourless lactone diethyl salt.

The remarkable colour-change which takes place when the colourless phenolphthaleïn is converted into its alkali salt is also considered by Bernthsen and Friedländer to be due to a change from a lactone to a quinone structure

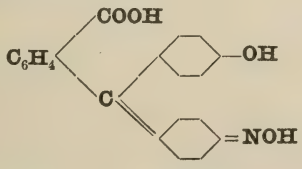


(Lactone form).



(Quinone form).

There is, however, no direct evidence of the existence of this substance in a quinone form, the phenolphthaleïnoxime



which was prepared by Friedländer in support of his view, having been shown to possess another constitution.

Further, Herzig and Meyer prepared a colourless lactone ethyl salt by alkylating phenolphthaleïn in alkaline solution, that is, in that condition in which it is assumed to possess a quinone structure; and Bistrzycki and Nencki, under the same conditions, also prepared a colourless benzoyl derivative by the action of benzoyl chloride.

The exact behaviour of phenolphthaleïn with alkalies is as follows:—

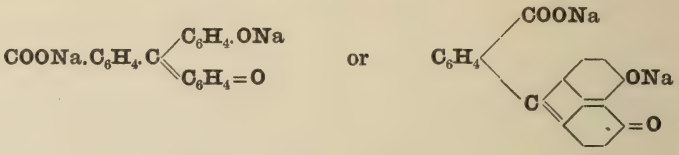
When the alkali is first added to a colourless solution of phenolphthaleïn in dilute alcohol, an intense red coloration is produced, which disappears on the addition of excess of alkali or of alcohol.

This behaviour was explained by Ostwald (*Wissenschaftl. Grundlagen der analyt. Chemie*, II^te Aufl., p. 116) on the theory of electrolytic dissociation, by which it was supposed that whilst phenolphthaleïn itself and its undissociated salts are colourless, its ions are red, and that the disappearance of the colour on adding an excess of alkali or alcohol denotes the suppression or retrogression of ionisation.

This view was adopted by Herzig and Richard Meyer (Herzig, *Ber.*, 1895, xxviii. 3258; 1896, xxix. 138; R. Meyer, *Jahrbuch d. Chem.*, 1899, ix. 404), by O. Fischer (*Zeit. Farb. Ind.*, 1902, i. 281), and by R. Meyer and O. Spengler (*Ber.*, 1903, xxxvi. 2949).

That the behaviour of phenolphthaleïn towards alkali is open to explanation by means of the quinonoid theory is evident from the later work of R. Meyer and his co-workers (*Ber.*, 1905, xxxviii. 1318; 1908, xli. 2446; 1911, xliv. 1954) taken in conjunction with that of Green and Perkin (*J.C.S.*, 1904, lxxxv. 398).

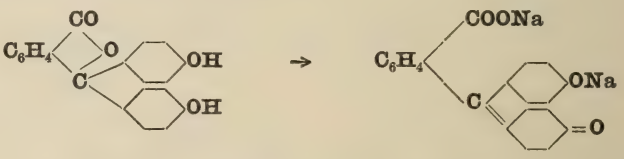
R. Meyer finds that the red sodium compound of phenolphthaleïn has the formula $C_{20}H_{12}O_4Na_2$, and that its structure can therefore be represented thus



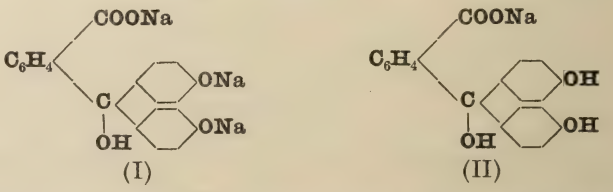
On the other hand, Green and Perkin show that when the colourless solution formed by the addition of excess of alkali is neutralised by acetic acid, it contains an alkali salt of the formula $C_{20}H_{15}O_5K$.

It is evident, therefore, that the course of these changes can be represented thus—

(1) Alkali acts on the solution of the colourless lactone form, producing the red alkali compound of the quinone type

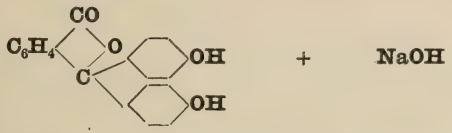


(2) The further action of alkali leads to the addition of the elements of the hydroxide forming the colourless carbinol salt of the formula (I)



(3) When the excess of alkali is neutralised by acetic acid the feebly acid phenol hydroxyls are restored and the colourless solution then contains the salt $C_{20}H_{15}O_5Na$ (II).

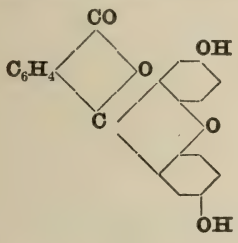
(4) When the colourless solution of this salt is boiled it becomes deep-red, and a precipitate of phenolphthaleïn separates. It follows that in these circumstances the carbinol salt is decomposed into lactone phenolphthaleïn and free alkali.



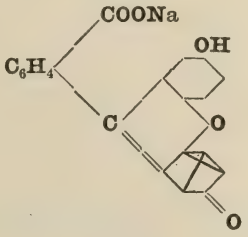
and that the alkali set free then reacts with an equivalent quantity of the liberated phenolphthaleïn to form the coloured disodium salt.

The main difficulty in assigning the quinone structure to these salts arises from the fact that it is not easy to explain the precisely similar behaviour of hydroquinonephthaleïn upon the same lines.

Hydroquinonephthaleïn is formed from hydroquinone and phthalic anhydride, and in its colourless lactone form has the structure (III)

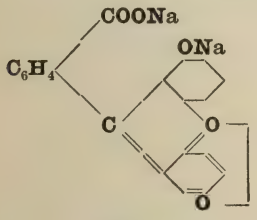


(III)

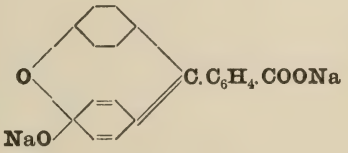


(IV)

It forms a violet alkali salt of the formula $C_{20}H_{10}O_5Na_2$, to which R. Meyer assigns the meta-quinonoid structure (IV), but which Green and Perkin regard as an orthoquinone derivative, which, written as the disodium salt, would be (V).



(V)



(VI)

Other suggestions have been advanced by v. Baeyer (*Ann.*, 1910, cccIxxii. 133) and by Kehrmann (*ibid.*, 337), but the views of these chemists are not in accordance with the established formula of the coloured salt (compare R. Meyer and Posner, *Ber.*, 1911, xliv. 1954).

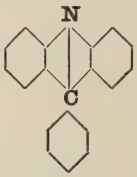
Acree and his co-workers (*Amer. Chem. J.*, 1908, xxxix., 528, 789; 1909, xlii., 115) consider that the cause of colour is not quinonoid in the strict sense of the term, but that it is due to the presence of a quinone phenol group $OK.C_6H_4.C:C_6H_4:O$. They regard the ultimate cause of colour as due to the presence of a tautomeric salt (VI) formed by the intramolecular rearrangement between the CO of the quinone group and the phenolic ONa.

Other views on this question are expressed by Silberrad (*J.C.S.*, 1906, lxxxix. 1793; *Proc.*, 1908, 209; see also Green, *Proc.*, 1907, 12; 1908, 206).

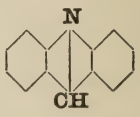
CHAPTER XVI.

ACRIDINE DYESTUFFS.

To this group belong a few technically important dyestuffs, which are amido-derivatives of phenylacridine and of acridine



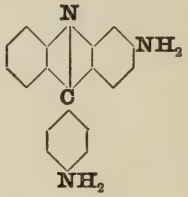
(phenylacridine).



(acridine).

Mention has already been made of a dyestuff of this group—*Chrysaniline*—which was discovered by Nicholson in the mother liquors of Magenta prepared by the arsenic acid method.

This substance is a diamidophenylacridine of the constitution (Fischer and Körner, *Ber.*, 1884, xvii. 203)

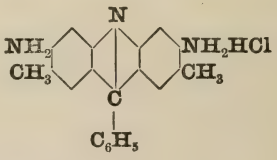


and its mode of formation is given on p. 90.

The impure product occurs in commerce under the name of Phosphine, a yellow basic dyestuff which is largely used for the dyeing of leather.

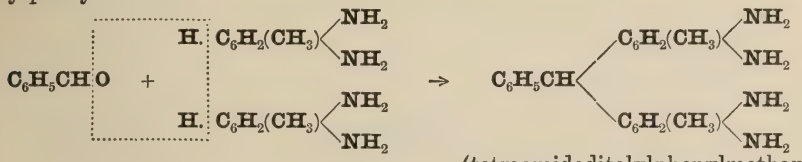
In 1887 Rudolph (E.P. 9614[88], A.P. 382,832) discovered other dyestuffs of this group, which are prepared by the condensation of an aldehyde with a *m*-diamine, elimination of ammonia from the product, and subsequent oxidation.

An instance may be given in Benzoflavine [O]



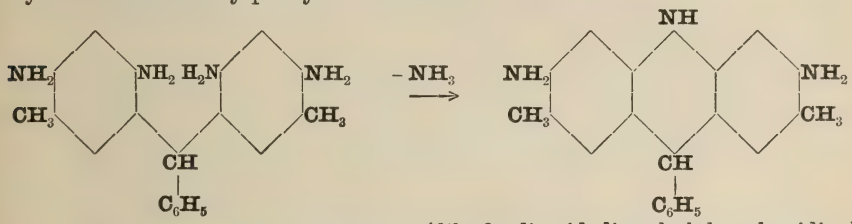
which is prepared in the following way :—

(1) Benzaldehyde is condensed with *m*-toluylenediamine to form tetraamidoditolylphenylmethane



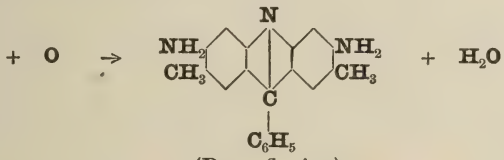
(tetraamidoditolylphenylmethane).

(2) When this is treated with hydrochloric acid, ammonia is split off and dihydrodiamidodimethylphenylacridine formed



(dihydrodiamidodimethylphenylacridine).

(3) The dyestuff is then formed from this on oxidation

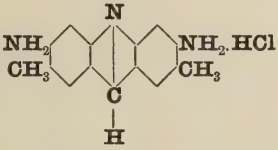


(Benzoflavine).

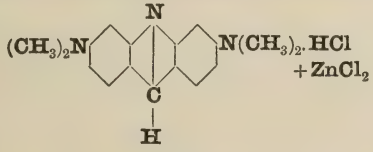
As a basic dyestuff Benzoflavine finds considerable application in the dyeing of wool, silk, and cotton (tannin mordant), yellow.

Similar dyestuffs are :—

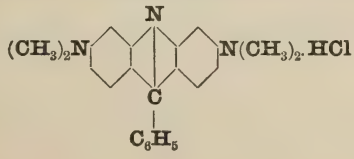
Acridine yellow [L], from formaldehyde + *m*-toluylenediamine



Acridine orange [L], from formaldehyde + *m*-amidodimethylaniline



and Acridine orange R extra [L], from benzaldehyde + *m*-amidodimethylaniline



CHAPTER XVII.

ANTHRACENE DYESTUFFS.

For the sake of convenience it is desirable to divide these colouring matters into three groups, viz :—

(1) Oxyketone dyestuffs.

(2) Colours derived from amino-oxy- and arylamino-derivatives of anthraquinone.

(3) Vat colours derived from anthraquinone.

(1) Oxyketone Dyestuffs.

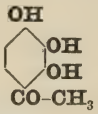
The dyestuffs of this group contain an aromatic ring in which two ortho-hydroxy-groups are in the ortho-position to a carbonyl group.

They are, therefore, mordant dyestuffs forming coloured lakes with various metallic oxides, which are characterised by possessing remarkable fastness to both light and washing.

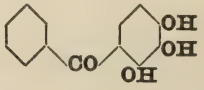
Although the most important dyestuff of this group is Alizarine, yet there are a few other dyestuffs, not derivatives of anthracene, which are classed with Alizarine owing to the many properties they have in common with it.

To these belong :—

Alizarine yellow C [B], which is prepared by the action of acetic acid and zinc chloride on pyrogallic acid, and has the formula

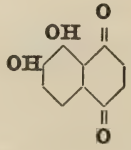


Alizarine yellow A [B], from benzoic acid or benzoylchloride and pyrogallic acid



and *Alizarine black* S [B], which is prepared by heating dinitronaphthalene with a solution of sulphur in fuming sulphuric acid, and treating the dioxynaphthoquinone which is thus formed with sodium bisulphite.

Its formula (ketone) is

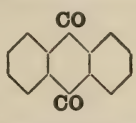


(Naphthazarine).

The chromium lake of this dyestuff is black.

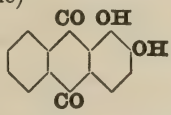
Alizarine Dyestuffs.

To this class belong a series of dyestuffs which are derivatives of anthraquinone



containing two ortho-hydroxyl groups in the ortho-position to one of the carbonyl groups (see *Law of Liebermann* and *v. Kostanecki*, p. 42).

Alizarine (dioxyanthraquinone)



was originally prepared from the madder root (*Rubia tinctorum*, L.), in which it occurs in the form of a glucoside, ruberythric acid, which can be converted into a sugar and Alizarine on boiling with dilute acids. Since 1868, however, it has been prepared by synthetic means.

The madder cultivation was a very considerable industry, and in the year 1868 as much as 70,000 tons of madder were produced from the various countries in which it was grown.

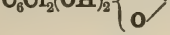
In this year Graebe and Liebermann made the epoch-making discovery that the chief madder dyestuff, Alizarine, was a derivative of anthracene, since it could be converted into this hydrocarbon by distillation with zinc dust, a method of reduction which had been discovered shortly before by Baeyer (*Ann.*, 1866, cxl. 295).

In the same way Graebe and Liebermann also found that the dyestuff Purpurine, which accompanies Alizarine in madder, gave anthracene on distillation with zinc dust.

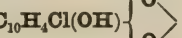
Before this time, however, a considerable amount of work had been done on Alizarine with the object of determining its constitution, and between 1848 and 1852 many papers were published by Schunck, Schunck and Gerhardt, Wolff and Strecker, etc., with the result that Alizarine was considered to be a derivative of naphthalene.

At this time the quinones were still undiscovered, and in 1868 Graebe (*Ann.*, 1868, cxlvi. 30) published a paper on their investigation.

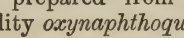
He found that *chloranilic* acid, $C_6H_2Cl_2O_4$, prepared by the action of alkalies on *chloranil*, $C_6Cl_4O_2$, did not contain a carboxyl group like other organic acids, but that it was a *dioxydichlorquinone*, which he formulated thus :—



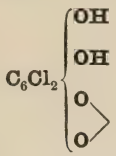
In the same way he found that the similarly constituted chloroxynaphthalinic acid was a *chloroxynaphthoquinone*



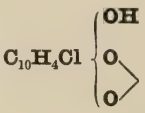
and that a compound of the formula $C_{10}H_6O_3$, which Martius and Griess (*Ann.*, 1865, cxxxiv. 376) had prepared from naphthalene, and which they mistook for Alizarine, was in reality *oxynaphthoquinone*



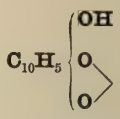
The analogy in behaviour between chloranilic acid, chloroxynaphthalinic acid, and Alizarine, and the fact already mentioned, that this latter substance gave anthracene on dry distillation with zinc dust, led Graebe and Liebermann (*Ber.*, 1868, i. 49) to the assumption that Alizarine was a dioxyanthraquinone and Purpurine a trioxyanthraquinone



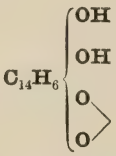
(Chloranilic acid).



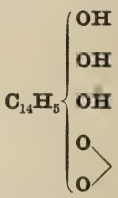
(Chloroxynaphthalinic acid).



(Oxynaphthoquinone).

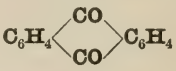


(Alizarine).



(Purpurine).

These formulæ were subsequently modified by the discovery of Zincke and Fittig that anthraquinone was a diketone of the formula



Continuing their investigations, Graebe and Liebermann found that the compound previously prepared by Laurent by the direct oxidation of anthracene was identical with anthraquinone. In order to convert this into a dioxy-derivative, they transformed it first into a dibromo-derivative, and then, by fusing with potash, produced a dioxyanthraquinone identical with the Alizarine from the madder root.

This, the first synthetic preparation of a natural dyestuff, was applied on the technical scale by the Badische Anilin und Soda Fabrik, but from the first considerable difficulty was experienced in preparing sufficient pure anthracene for the purpose.

It was soon found, however, that Alizarine could be much more readily prepared from anthraquinone monosulphonic acid.

Some time previously Graebe and Liebermann had attempted, but without success, to prepare sulphonic acids of anthraquinone by sulphonation, and it was first pointed out by Caro that on treating anthraquinone with sulphuric acid at 200° a sulphonic acid was formed, which, on fusion with potash, yielded Alizarine.

Practically at the same moment the identical reaction was discovered by W. H. Perkin in England.

The patent application of Caro, Graebe, and Liebermann bears the date 25th June 1869; that of W. H. Perkin, 26th June 1869.

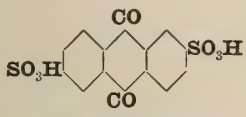
Another method for the preparation of anthraquinone disulphonic acid was again discovered, practically simultaneously, by Graebe and Liebermann (*Ann.*, 1871, clx. 137) and by W. H. Perkin (*Ann.*, 1871, clviii. 319), and patented by the latter on 17th November 1869.

This method consists in treating dichloro- or dibromo-anthracene with sulphuric acid, thus converting it into dichloro- or dibromo-anthracene disulphonic acid, which, on further treatment with sulphuric acid (*Graebe, Liebermann*, and *Perkin*), or by oxidation with MnO_2 (*Perkin*), is transformed into anthraquinone disulphonic acid.

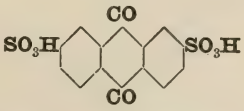
On fusion with potash this disulphonic acid yields Isopurpurine.

The disulphonic acids of anthraquinone are, however, at the present day prepared by direct sulphonation with sulphuric acid containing 40 per cent. of anhydride at 280–350° C. (*Koch*).

In this way two sulphonic acids are formed



(α-anthraquinone disulphonic acid).

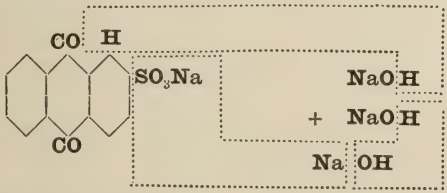


(β-anthraquinone disulphonic acid).

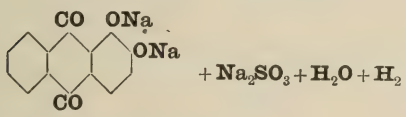
On fusion with caustic soda, the former yields Flavopurpurine; the latter Iso- or Anthra-purpurine.

When Alizarine was first prepared from anthraquinone sulphonic acid, it was thought that the disulphonic acid alone reacted. It was soon discovered, however, that only the β-monosulphonic acid is capable of yielding Alizarine with potash, the disulphonic acid being converted into trioxy-derivatives of anthraquinone.

The equation representing the formation of Alizarine is evidently as follows :—



(sodium β-anthraquinone monosulphonate).



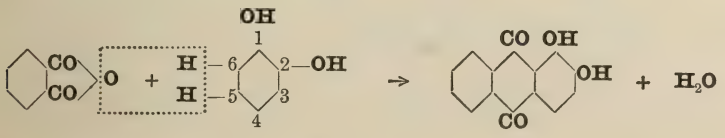
(sodium salt of Alizarine).

The discovery of the true nature of the reaction explained the loss of Alizarine experienced in the early days of the industry, which was evidently caused by the reduction of the anthraquinone by nascent hydrogen.

This is now obviated by the addition of sodium chlorate to the melt (*Koch*).

The positions of the hydroxyl groups in Alizarine and Purpurine have been determined in the following way (*Baeyer* and *Caro*) :—

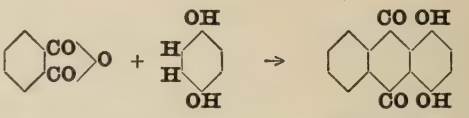
(1) Phthalic anhydride on condensation with pyrocatechol in concentrated sulphuric acid solution yields Alizarine



From this synthesis it follows that the two hydroxyl groups are in the ortho-position to one another.

It, however, does not determine their position with reference to the carbonyl groups, since the condensation might have taken place in the positions 4, 5 instead of 5, 6.

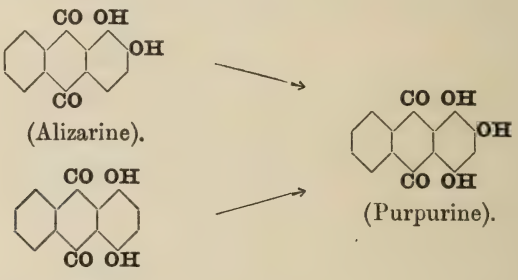
(2) Phthalic anhydride in the same way condenses with hydroquinone to form Quinizarine



(Quinizarine).

(3) Both Alizarine and Quinizarine yield Purpurine on oxidation.

The only formulæ in accordance with these facts are those given in the following equations:—



(Alizarine). (Purpurine).

(Quinizarine).

Alizarine is insoluble in cold water, and is always met with in the form of a paste.

This formerly consisted of 10 per cent. of Alizarine suspended in water, but is now made almost exclusively of 20 per cent. strength. The price of 10 per cent. paste in 1870 was 6s. to 7s. per lb., and in 1914 for 20 per cent. paste 5½d. per lb.

In this paste form Alizarine is sufficiently finely divided to be appreciably soluble in hot water; when once dry, however, it loses this property, and then is not well adapted for the purposes of dyeing and printing.

For transhipment, Alizarine is frequently made in the form of a powder, which is dissolved in caustic soda and reprecipitated by hydrochloric acid by the dyer at its destination.

It is also prepared in the form of a powder mixed with starch; when placed in water the starch swells and the powder is converted into a thin paste suitable for the dyer.

The mordant dyestuffs can be divided into two classes,

(1) Polygenetic dyestuffs,
(2) Monogenetic dyestuffs,

the former yielding different-coloured lakes with different mordants, the latter yielding the same coloured lake whatever the nature of the mordant employed.

Alizarine is a polygenetic dyestuff in the widest sense of the term, and gives the following series of colours with the mordants named:—

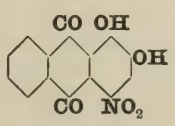
Magnesium,	violet.
Calcium,	purple-red.
Barium,	purple-red.
Strontium,	red-violet.
Aluminium,	rose-red.
Chromium,	brown-violet.
Iron (ferrous),	black-violet.
Iron (ferric),	brown-black.
Copper,	brown-violet.
Lead,	purple-red.
Tin (stannous),	red-violet.
Tin (stannic),	violet.
Mercury,	black-violet.

In actual practice only the aluminium, iron, tin, and chromium lakes are employed.

The methods of applying Alizarine to the fibres are dealt with on p. 326.

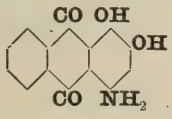
Derivatives of Alizarine.—*Nitro*-derivatives.—Of the six theoretically possible nitroalizarines, only two have been thoroughly investigated.

α-Nitroalizarine



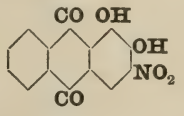
was originally prepared by Perkin by the action of nitric acid on diacetylalizarine.

It is itself of no importance as a dyestuff, but on reduction is converted into *α-amidoalizarine*



which is found in commerce under the names *Alizarine garnet* R [M] and *Alizarine cardinal* [By].

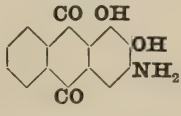
β-Nitroalizarine—Alizarine orange



was first prepared in 1874 by Strobel by treating material which had been dyed with Alizarine, with nitrous acid fumes.

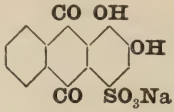
It can also be prepared by the direct nitration of Alizarine, and is a powerful dyestuff, forming orange lakes with alumina, and red-violet with iron salts.

On reduction it is converted into *β-amidoalizarine—Alizarine maroon* [B]



which forms a red lake with alumina and grey with iron.

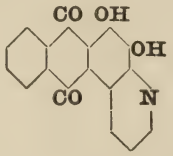
Alizarine red S [B] is alizarine monosulphonic acid, and is prepared by the direct sulphonation of Alizarine. Its formula is



It is chiefly used for the dyeing of mordanted wool.

Alizarine blue [B]. — This important dyestuff was first prepared by Prud'homme by heating β-nitroalizarine (Alizarine orange) with glycerine and sulphuric acid.

The determination of the constitution of this substance is due to Graebe (*Ann.*, 1880, cci. 333), who found it to be an anthraquinoline of the formula



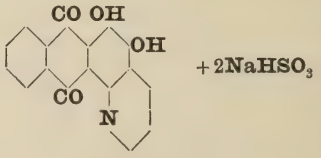
Subsequently, the formation of a quinoline derivative in this reaction was confirmed by Skraup, who prepared quinoline by heating a mixture of aniline and nitrobenzene with glycerine and sulphuric acid.

At the present day Alizarine blue is made in a similar way, viz., by heating a mixture of nitro- and amidoalizarine with glycerine and sulphuric acid at 105° C.

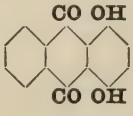
Alizarine blue is only feebly polygenetic, and gives blue lakes with most mordants. The most important is the Chromium lake.

Alizarine blue S is the sodium bisulphite compound of Alizarine blue, and is the most usual form in which Alizarine blue is met with in commerce.

Alizarine green S [M] is the sodium bisulphite compound of the corresponding α-alizarine quinoline, and is prepared from α-amidoalizarine. Its formula is



Isomerides of Alizarine.—*Quinizarine*

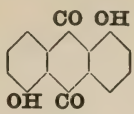


which is manufactured by oxidising anthraquinone by means of fuming sulphuric acid in the presence of boric acid or by means of sodium nitrite, is of no importance as a dyestuff by itself, since, owing to the positions of the hydroxyl groups, it does not combine with mordants to form lakes.

It is, however, converted into valuable acid dyestuffs on condensation with primary aromatic amines and subsequent sulphonation. Such dyestuffs are Alizarine cyanine green, Kymric green, and Alizarine pure blue.

They are without mordant properties.

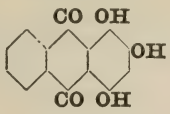
Anthrarufine



is formed, according to Schunck and Römer (*Ber.*, 1878, xi. 1176), when *m*-oxybenzoic acid is treated with sulphuric acid, or (Liebermann and Böck, *Ber.*, 1878, xi. 1616) by oxidising anthracene-β-disulphonic acid, and fusing the anthraquinone disulphonic acid thus formed, with potash.[1]

It is the parent substance of the important blue acid wool dye, Alizarine sapphirol [By] (Solway blue), which is diamidoanthrarufine disulphonic acid.

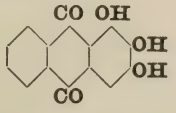
Trioxyanthraquinones.—*Purpurine* [B]



accompanies Alizarine in Madder, and is formed synthetically either by the oxidation of Alizarine or of Quinizarine.

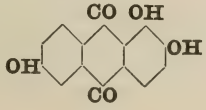
Its lakes with mordants are very similar in shade to those formed from Alizarine.

Anthracene brown [B] (Anthragallol)

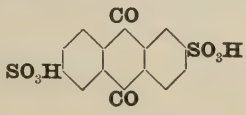


is formed (Seuberlich, *Ber.*, 1877, x. 38) on heating gallic acid and benzoic acid with sulphuric acid. Its chromium lake is brown.

Flavopurpurine (Alizarine X [By]), (Alizarine GI or RG [B])



is prepared by fusing the α-disulphonic acid of anthraquinone

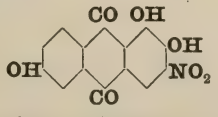


with potash.

It is very similar in its properties to Alizarine.

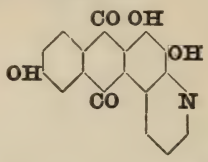
Alizarine SSS is the sulphonic acid (sodium salt), and is an important wool dye.

Alizarine orange G [M] is the β-nitro-derivative



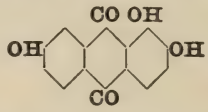
[1] Anthrarufine is manufactured from anthraquinone-1 : 5-disulphonic acid by heating it with lime under pressure.

From this, on treatment with glycerine and sulphuric acid, the quinoline-derivative *Alizarine black* P [M] is produced

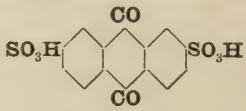


The bisulphite compound is Alizarine black S [M].

Isopurpurine (Alizarine GD [M]), (Alizarine RX [M]), (Alizarine SX extra [By])



is prepared by the fusion of the β-disulphonic acid of anthraquinone



with caustic soda.

It is similar in its properties to the other members of this group.

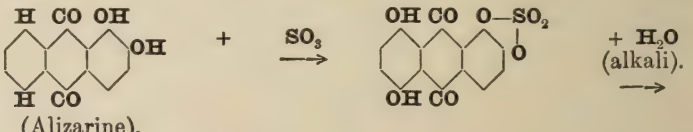
As a wool dye it is used in the form of its sulphonic acid, the sodium salt of which is Alizarine SS.

Tetraoxyanthraquinones.—In 1890 Bohn (*Ber.*, xxiii. 3739) made the important discovery that by the action of fuming sulphuric acid on anthraquinone and anthraquinoline derivatives, new hydroxyl groups could be introduced.

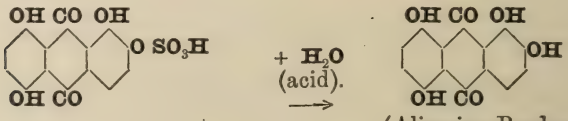
This reaction, which takes place better in the presence of boric acid, was further developed by R. E. Schmidt, with the result that a large number of polyoxy-derivatives of Alizarine and of Alizarine blue have been prepared.

Sulphuric acid ethers (or boric acid ethers), which are intermediate products in this reaction, furnish the free polyoxy-derivatives on hydrolysis with acids, the new groups entering, when possible, in the para-position of the unsubstituted ring.

Thus the oxidation of Alizarine to *Alizarine Bordeaux* B [By], through the agency of fuming sulphuric acid containing 80 per cent. SO_3, takes place in three stages



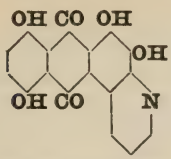
(Alizarine).



(Alizarine Bordeaux).

Alizarine Bordeaux forms claret lakes with aluminium, and violet-blue with chromium salts. Another colour of the same type is

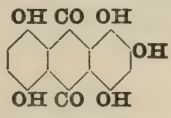
Alizarine green S [B], sodium bisulphite compound of



which is prepared by treating Alizarine blue with fuming sulphuric acid.

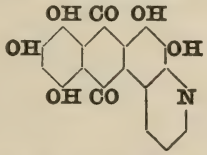
It is an important wool dye, forming a blue-green lake with chromium.

Pentaoxyanthraquinones.—*Alizarine cyanine* R [By]



prepared by the oxidation of Alizarine Bordeaux with manganese dioxide and sulphuric acid, forms a blue chromium lake much used in wool-dyeing.

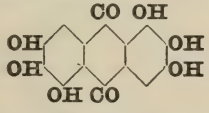
Alizarine indigo blue S [B], sodium bisulphite compound of



is prepared by acting upon Alizarine green with sulphuric acid at 200°.

The chromium lake is indigo blue in colour.

Hexaoxyanthraquinones.—*Rufigallol* [B]



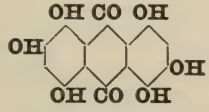
was first prepared by Robiquet (*Ann.*, 1836, xix. 204) by heating gallic acid with concentrated sulphuric acid at 140°. Its constitution was determined by Klobukowsky.

It is a polygenetic dyestuff, forming with

Aluminium	. .	red,
Iron	. . .	violet, and
Chromium	. .	brown lakes.

The shades, however, are not pure in tone.

Anthracene blue WR [B]



is prepared (E.P. 19,589[91], 13,029[92], A.P. 502,603) by heating 1 : 5 dinitroanthraquinone with fuming sulphuric acid (40 per cent. SO_3) with or without a reducing agent, and treating the sulphuric ether which is formed with ordinary sulphuric acid.

It is a wool dye, giving violet lakes with aluminium, and blue with chromium.

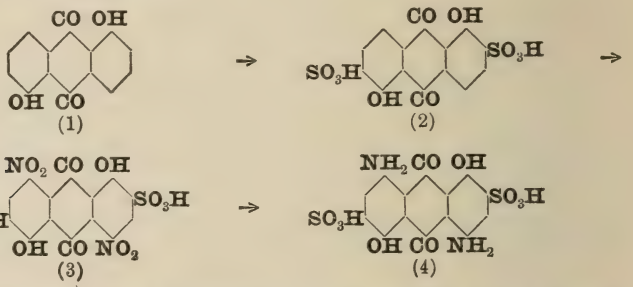
A disulphonic acid of this dyestuff is *Acid alizarine blue*, BB and GR [M].

(2) Colours derived from Amino-oxy- and Arylamino-Derivatives of Anthraquinone.

The action of ammonia on the polyhydroxy-derivatives of anthraquinone leads to a partial replacement of the hydroxyl-groups by amino-groups, and consequently to the formation of new colouring matters. An example of this kind is *Alizarine cyanine* G, which is produced by the action of ammonia on Alizarin cyanine R (*q.v.*), and which, in the form of its greenish-blue chromium lake, is much used in wool-dyeing.

Colouring matters of still greater importance, which are, moreover, both acid and mordant dyestuffs, are produced from anthraquinone derivatives by a process involving sulphonation, nitration, and reduction. A good example of this class is :—

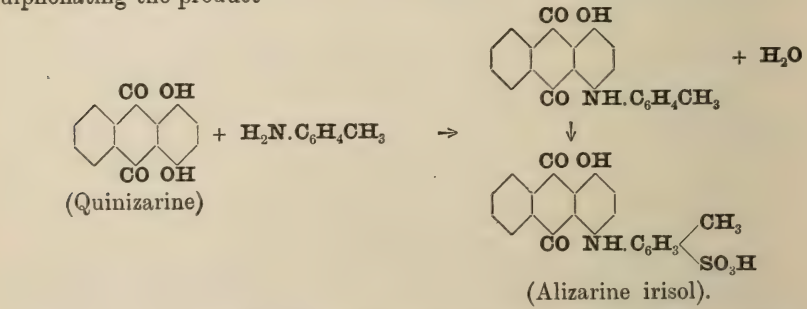
Alizarinesaphirol, a compound which is prepared from anthrarufine (1) by first sulphonating it to anthrarufine disulphonic acid (2), nitrating this to dinitro-anthrarufine disulphonic acid (3), and finally converting this compound into diaminoanthrarufine disulphonic acid (4) by reduction. Alizarinesaphirol is the sodium salt of this sulphonic acid.



Alizarinesaphirol dyes wool a pure shade of blue from an acid bath, and produces greenish-blue shades on chrome-mordanted wool.

Similar colouring matters are produced from hydroxy-derivatives of anthraquinone by heating them in the presence of a condensing agent, such as boric acid, with certain primary aromatic amines. Thus :—

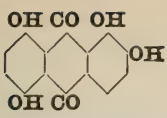
Alizarine irisol is produced by the action of *p*-toluidine on quinizarine and sulphonating the product

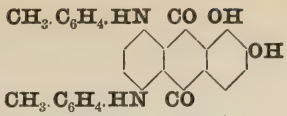


(Alizarine irisol).

Alizarine irisol gives fast violet-blue shades on chrome-mordanted wool. Another important colour of this group is :—

Alizarine viridine, which is produced from Alizarine Bordeaux by condensation with *p*-toluidine

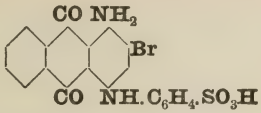

(Alizarine Bordeaux).


(Alizarine viridine).

Chrome-mordanted wool is dyed a fast green by this colouring matter.

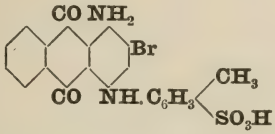
Although the mordant properties of anthraquinone derivatives are entirely absent when the hydroxy-groups in the molecule are wholly displaced, yet important acid colouring matters are produced as sulphonic acids when arylamino-residues enter the anthraquinone complex. The following colouring matters illustrate this statement:—

Alizarine pure blue is



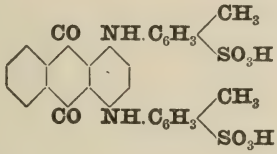
and

Alizarine blue GG is the higher homologue



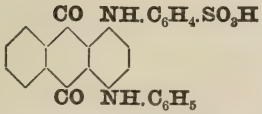
both these compounds dye wool a pure shade of blue from an acid bath. Similar compounds are:—

Alizarine cyanine green



and

Anthraquinone green GX



both of which dye wool a clear, fast shade of green from an acid bath.

(3) Vat Colours derived from Anthraquinone.

The great fastness of colours produced by the vat process of dyeing (see pp. 37 and 324), has caused many research chemists to direct their attention towards the production of dyestuffs of this type, and within recent years a large number of important colouring matters have been introduced into commerce.

Indigo, the greatest of all colouring matters, was for many years the sole representative of this group, and after the structure of indigo had been definitely established, it was evident that the work of research chemists would be directed upon two lines, viz. in the first place, to prepare derivatives of indigo; and, secondly, to isolate substances having similar properties. For many years both

branches of research were fruitless, and it was not until the year 1901 that the first technically important halogen derivative of indigo, viz. 5 : 7 : 5′ : 7′—tetrachloroindigo—was prepared by the Badische Anilin und Soda Fabrik. Since that time many derivatives of this type have been prepared, and a description of them is given in a later chapter (see p. 187). Finally, the discovery of the sulphur analogue of indigo, Thioindigo, by Friedländer in 1906 greatly widened this field of research.

The search for vat colouring matters having a different structure from that of indigo was successful in the year 1901, when R. Bohn prepared Indanthrene by fusing 2-aminoanthraquinone with potash. Since that date the number and importance of the colouring matters of this type have increased so rapidly that at the present time they may be said to be the most important series of colours that the dyer has at his disposal.

There is, however, one important difference between the vat colours of the indigo class and those of the indanthrene series: for whereas the vats formed by the reduction of indigo and its derivatives are colourless or at most pale yellow, the hydro derivatives of members of the indanthrene series are themselves coloured substances, which are substantive in alkaline solution to the cotton fibre; hence the vats derived from the members of these series are always intensely coloured.

For the sake of convenience it is advisable to divide the members of this series into five classes (Bohn, *Ber.*, 1910, xliii. 998), viz. :—

1. Indanthrene.
2. Flavanthrene.
3. Benzanthrone colours.
4. Anthraquinoneimides.
5. Acyl derivatives of aminoanthraquinone.

1. *Indanthrene* [B], *Chloranthrene blue* B.D. [H], *Duranthrene blue* [Claus & Co.], *Caledon blue* [Solway Dyes Co.].—Literature: E.P. 3239[01], 12,185[01], 22,762[01], A.P. 682,523; Scholl and others (*Ber.*, 1903, xxxvi. 3410, 3427, 3710; 1907, xl. 320, 326, 390, 395, 924, 933); Bohn (*Ber.*, 1903, xxxvi. 1258; 1910, xliii. 999); and Kaufler (*Ber.*, 1903, xxxvi. 930, 1721).

Formation.—When 2-aminoanthraquinone is fused with potash at 200–300° (see preparation, p. 284), the blue soluble potassium salt of the hydro derivative of indanthrene is formed; the action of air on this solution precipitates the insoluble colouring matter. Alizarine is also formed in this reaction (compare Liebermann, *Ann.*, 1882, ccxii. 63), especially if the fusion with potash is carried out at a lower temperature (150–200°).

At a higher temperature the alizarine is converted into a brown product soluble in alkali, but in either case indanthrene can be readily isolated owing to its insolubility in alkali. Indanthrene produced in this manner is not a homogeneous substance, but is a mixture of two blue compounds, indanthrene A and indanthrene B, the latter being worthless as a colouring matter. The two compounds differ from one another in their solubility in aniline, quinoline, and in nitrobenzene, indanthrene A being less soluble than indanthrene B. Both products form hydro derivatives on reduction which can be distinguished by the difference in the solubility of their alkali salts in water.

It is, however, possible so to arrange the experimental conditions that either indanthrene A or indanthrene B is the chief product. For example, if the fusion is carried out in the presence of oxidising agents, such as potassium nitrate, indanthrene A is the chief product, and indanthrene B is only formed in a very small amount. On the other hand, when a reducing agent is present, indan-

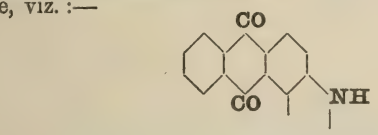
threne B is the chief product; thus indanthrene B is formed when 2-aminoanthraquinone is heated with alcoholic potash at 140–150°.

When 2-aminoanthraquinone is fused with potash at a still higher temperature (330–350°), the yellow colouring matter flavanthrene is formed (*q.v.*).

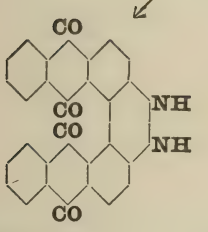
Constitution.—The analysis of indanthrene, and the determination of its molecular weight by the boiling-point method in quinoline, show it to possess the empirical formula $C_{28}H_{14}O_4N_2$. It must therefore be formed from two molecules of 2-aminoanthraquinone by the loss of four atoms of hydrogen, thus :—

$$2C_{14}H_9O_2N - 4H = C_{28}H_{14}O_4N_2.$$

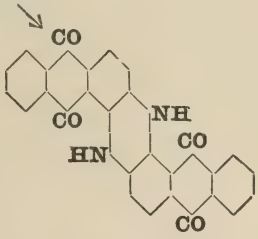
From the fact that indanthrene does not give on reduction either 2-aminoanthraquinone or a reduction product of this substance, it follows that it cannot be an azo derivative, and that the four hydrogen atoms eliminated are not those originally attached to the amino-groups of the two molecules of the parent substance. On the other hand, the absence of a free amino-group in indanthrene shows that both amino-groups must have taken part in the condensation, and the simultaneous formation of alizarine suggests that the joining of the two anthraquinone residues has taken place through the agency of the hydrogen atoms in the ortho-position to the amino-groups. There are then two possible formulæ for indanthrene, viz. :—



anthraquinone residue



(Ortho-diazine formula).



(Para-diazine formula).

Since indanthrene is not converted into a diamine on reduction, it cannot have the ortho-diazine formula. It must therefore be a para-diazine, that is, *N*-dihydro-1 : 2 : 2′ : 1′-anthraquinoneazine. The reactions of indanthrene are in complete accordance with this formula; moreover, several syntheses of the colouring matter have been effected which place the structure beyond question, and of these the following may be mentioned :—

(1) The condensation of 1 : 2-diaminoanthraquinone with 1 : 2-anthraquinone and subsequent oxidation and reduction (Lagodzinski, D.P. 170,562).

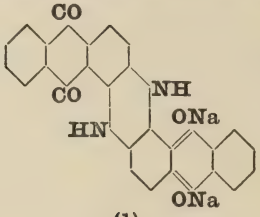
(2) The condensation of 1 : 2-aminohalogen anthraquinone with itself (Kugel, D.P. 158,287).

(3) The condensation of 1-aminoanthraquinone with itself through the agency of dilute acids under pressure (Isler, D.P. 186,636 and 186,637).

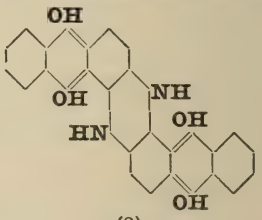
Properties.—Indanthrene is a dark indigo blue powder which is very sparingly soluble even in high boiling organic solvents. It can be obtained in the form of its characteristic curved needles, possessing a marked copper reflex, when the solution in boiling quinoline is cooled. It is one of the most stable substances known, and can be heated in the air at 470°, with concentrated hydrochloric acid at 400°, or with fused potash at 300°, without undergoing decomposition.

Sodium hypochlorite, which destroys the fastest colouring matters, merely oxidises indanthrene to the yellowish-green azine (see below), a substance which can be reconverted into indanthrene on reduction with sodium hydrosulphite.[1]

Reduction.—When indanthrene is reduced by sodium hydrosulphite in the presence of dilute caustic alkali, it is converted into a blue vat which contains the alkali salt of the dihydro-derivative in solution. Cotton steeped in this vat is dyed blue, since the dihydro-derivative is substantive to cotton; but when the dyed fibre is exposed to the air the dihydro-derivative is quickly oxidised to indanthrene. The formation of the vat with zinc dust leads to a yellowish-brown solution from which, however, indanthrene is also precipitated by the action of air. There is no doubt that the blue vat contains the disodium salt of *N*-dihydro-1 : 2 : 2′ : 1′-anthraquinoneanthrahydroquinoneazine (1), and that the yellow vat contains the sodium salt of *N*-dihydro-1 : 2 : 2′ : 1′-anthrahydroquinoneazine (2).



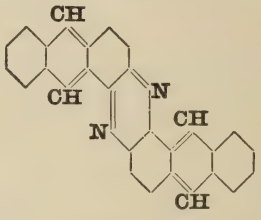
(1)



(2)

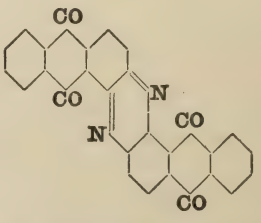
The disodium salt of formula (1), which crystallises from the blue vat on cooling, occurs in commerce under the name of *Indanthrene* S.

The complete reduction of indanthrene with phosphorus and hydriodic acid at 210–220°, or by distillation with zinc dust leads to anthrazine



and several intermediate products between this substance and indanthrene have been isolated by Scholl and his collaborators (*loc. cit.*).

Oxidation.—Indanthrene is a weak base and forms salts with strong acids which are dissociated by water. The two hydrogen atoms of the imido-groups are readily removed by oxidation, and the base is then transformed into the yellowish-green 1 : 2 : 2′ : 1′-anthraquinoneazine

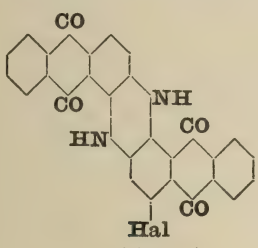


The azine is readily reduced to indanthrene, a change which can be effected by

[1] The technical term ; hyposulphite is more correct.

the action of direct sunlight. Thus cotton fibre which has been dyed with indanthrene, and subsequently treated with sodium hypochlorite solution to convert the blue compound into the yellow azine, will, on exposure to sunlight, be restored to its original colour. This reaction serves as a ready means of distinguishing fabrics dyed with indanthrene.

The Halogen Derivatives of Indanthrene.—The entrance of halogen atoms into the molecule of indanthrene changes the shade towards green; at the same time the sensitiveness of the hydroazine groups towards oxidising agents is considerably decreased. In order to introduce one halogen atom, indanthrene is, in the first instance, oxidised by nitric acid to anthraquinoneazine, and this substance, when heated with the halogen acid under pressure, is converted into the monohalogen derivative of indanthrene of formula (3)



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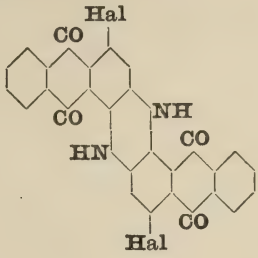


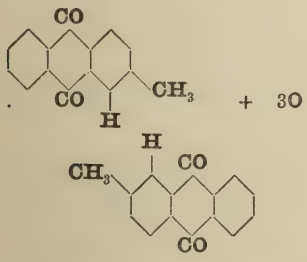
(4)

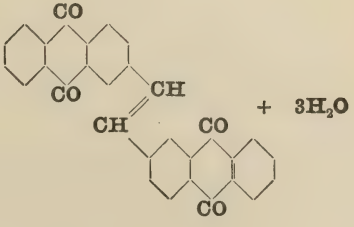
A second halogen atom can be introduced by oxidising the monohalogen derivative to the corresponding halogen derivative of anthraquinoneazine, and treating this with the concentrated halogen acid at a high temperature under pressure, the dihalogen derivative of indanthrene formed in this manner having the structure represented by formula (4).

The technically important halogen derivatives of indanthrene are:—

Indanthrene blue C or GC (E.P. 4035[02], A.P. 739,579), which is a mixture of di- and tri-bromoindanthrene, and is formed by the action of bromine on a solution of indanthrene in concentrated sulphuric acid at 60–80°, and *Indanthrene blue* GCD (E.P. 23,179[03], A.P. 753,659), a chloro-derivative which is produced in the form of the azine by boiling indanthrene with aqua regia. *Indanthrene blue* CE and *Algol blue* CF are also chloro-derivatives.

Anthraflavone G (Isler, E.P. 10,677[05], A.P. 837,840) is diphthaloylstilbene and not diphthaloylanthracene as formerly thought (*Ber.*, 1913, xlvi. 709, 712). It is formed by the oxidation of two molecules of 2-methylanthraquinone with lead oxide, thus:—





This substance dyes cotton a lemon shade of yellow, which is not fast to light; when mixed with indanthrene it yields, however, green shades, which are not surpassed in fastness by any other green colouring matter.

2. *Flavanthrene* (*Indanthrene yellow* [B], *Chloranthrene yellow* [H], *Caledon yellow* [Solway Dyes Co.]).—Literature: E.P. 24,354[01], A.P. 739,145; Scholl (*Ber.*, 1907, xl. 1691; 1908, xli. 2304); Scholl and Neovius (*ibid.*, 2534); Scholl and Mansfeld (*Ber.*, 1910, xliii. 1734).

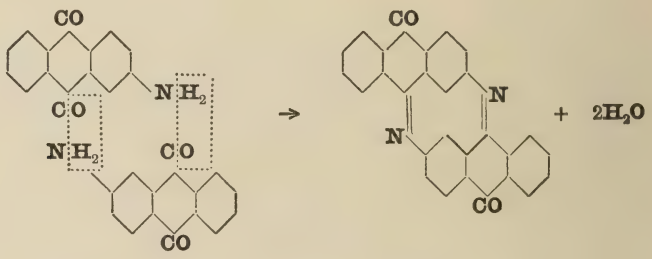
Formation.—Flavanthrene is produced by the fusion of 2-aminoanthraquinone with potash at 330–350°, and was originally isolated by Bohn in this manner. At the present time it is prepared technically by treating 2-aminoanthraquinone dissolved in boiling nitrobenzene with antimony pentachloride (see p. 285). It can also be prepared by the action of acid oxidising agents on 2-aminoanthraquinone (Kunz), and by the synthetic methods described in the next paragraph.

Constitution.—The elementary analysis of flavanthrene and the determination of the molecular weight of the oxygen free parent substance lead to the empirical formula $C_{28}H_{12}O_2N_2$. It is therefore derived from two molecules of 2-aminoanthraquinone in the following way:—

$$2C_{14}H_9O_2N = C_{28}H_{12}O_2N_2 + 2H + 2H_2O.$$

The elimination of water in the above reaction at once suggests interaction between the hydrogen atoms of two amino-groups and the oxygen atoms of two carbonyl groups of the two molecules of 2-aminoanthraquinone involved. On this assumption the course of the reaction may be represented as taking place in two stages, viz.:—

(1)



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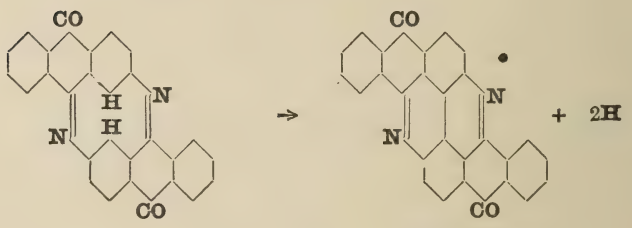
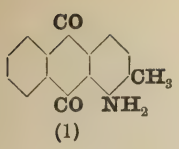


(Flavanthrene).

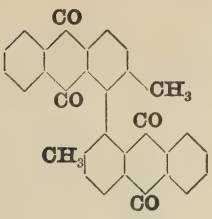
The hydrogen is not eliminated in the free state but reduces the colouring matter to the dihydro derivative (*q.v.*), the condition in which it occurs in the potash melt.

This structure for flavanthrene has been confirmed by its synthesis in two distinct ways, both of which are due to Scholl and his collaborators.

(1) 2-Methyl-1-aminoanthraquinone (1) is converted through the diazonium salt into the iodo-derivative and thence through the agency of copper powder into 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl (2). This substance is then oxidised to the dicarboxylic acid (3), and this is converted through the acid chloride into the acid amide (4). An attempt to prepare the amide (5) from the acid amide by the action of bromine and caustic alkali led to the production of flavanthrene.



(1)



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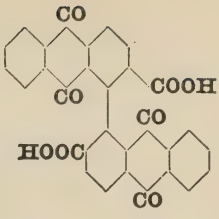

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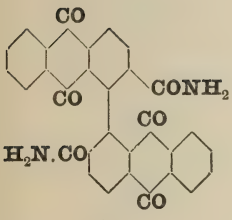
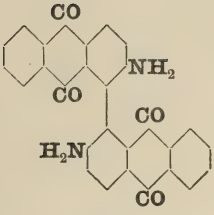
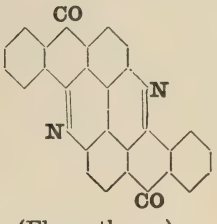


(4)

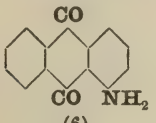


(5)

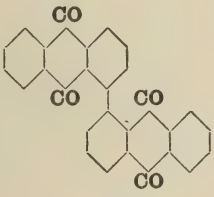


(Flavanthrene).

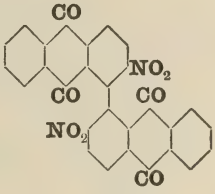
(2) 1-Aminoanthraquinone (6) is converted through the diazonium salt into the iodo-derivative, and this is transformed into 1 : 1′ or α-dianthraquinonyl (7) by the action of copper powder. Nitration partially converts this substance into the dinitro-derivative (8) which, on reduction with sodium sulphide, yields flavanthrene, the intermediate diamine (9) being spontaneously transformed into the colouring matter.



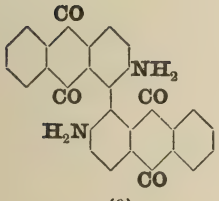
(6)



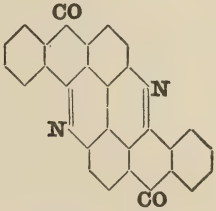
(7)



(8)



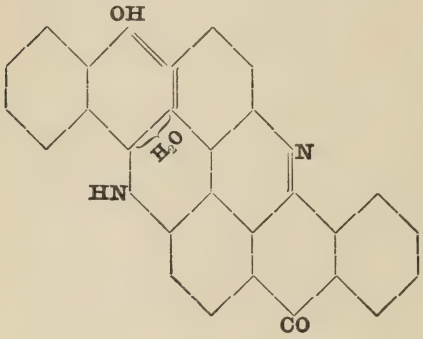
(9)

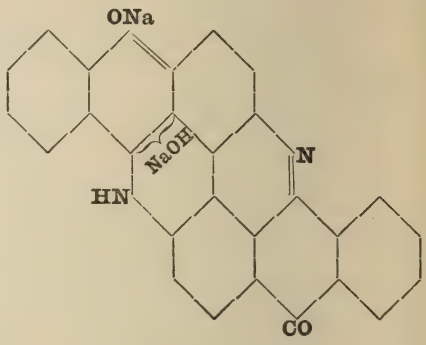


(Flavanthrene).

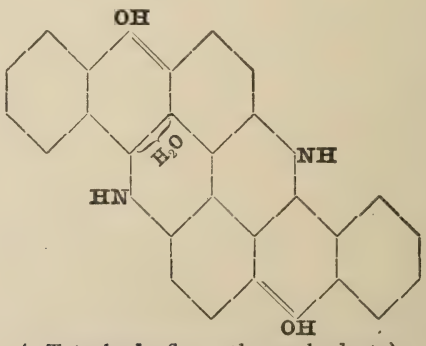
Properties and Reactions.—The treatment of flavanthrene with alkaline sodium hydrosulphite at 60–70° leads to the formation of a violet blue vat in which cotton is substantively dyed blue. When the fibre thus impregnated is exposed to the air, the blue colour rapidly changes to the brilliant yellow of flavanthrene. The violet blue vat contains the disodium salt of dihydroflavanthrene hydrate $C_{28}H_{14}O_2N_2,H_2O$, a substance which separates as a bluish-green precipitate on the addition of acetic acid. The constitution of this dihydro-derivative differs from the corresponding substance derived from indanthrene. The disodium

salt separates, as in that case, when the blue vat is allowed to cool, but it is not the disodium salt of the diphenol, and has a structure which is best represented by the expression $C_{28}H_{13}O_2N_2Na,NaOH$. That is to say, only one sodium atom is combined as phenolic salt, the other occurs as attached sodium hydrate in much the same manner as in the indigo vat (compare Binz, *Zeit. für angew. Chem.*, 1906, xxix. 1415). Thus it follows that not only is this sodium compound almost completely hydrolytically dissociated in the vat, but that it yields a monobenzoyl derivative with benzoyl chloride instead of the dibenzoyl derivative which would have been formed if the dihydro derivative had had the dihydroxylic structure similar to that of dihydro indanthrene. The constitution of dihydroflavanthrene hydrate and its sodium compound can therefore be represented by the following expressions:—





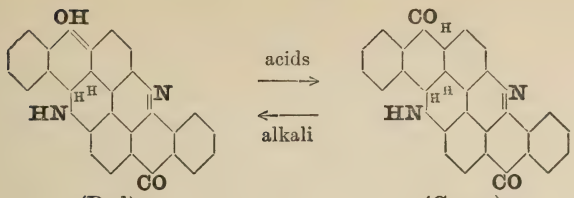
The reduction of flavanthrene with zinc dust and alkali leads to the formation of a brown vat which contains α-tetrahydroflavanthrene hydrate as its alkali salt. Another tetrahydro derivative, viz. β-tetrahydroflavanthrene, which does not form a hydrate, is produced by the action of phosphorus and hydriodic acid on flavanthrene at 170°. The α-derivative is so readily oxidised that it cannot be isolated in the free state, but when liberated from its salts passes at once into dihydroflavanthrene hydrate. The structure of this substance is therefore represented by the formula



(α-Tetrahydroflavanthrene hydrate).

The β-tetrahydro derivative, on the other hand, is exceedingly stable, and separates as a green precipitate when its red alkaline solution is acidified.

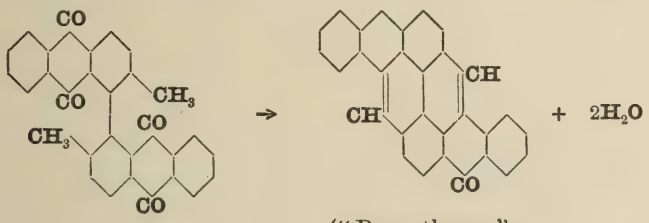
The colour change is probably due to desmotropism between the keto and enol forms, and may be represented by the expression



(Red). (Green).

The red alkaline solution of the β-derivative yields a yellow vat with zinc dust which contains β-hexahydroflavanthrene, $C_{28}H_{18}O_2N_2$.

Pyranthrene (*Indanthrene golden orange*), E.P. 14,578[05], 24,486[10], A.P. 856,811; *Ber.*, 1910, xliii. 346; 1911, xliv. 1448.—This important orange vat colour has a constitution similar to that of flavanthrene, but has two methine groups in place of the nitrogen atoms. The compound is formed by the intramolecular condensation of 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl (compare *Ber.*, 1907, **xl.** 1691) in accordance with the scheme



("Pyranthrene" —Pyranthrone).

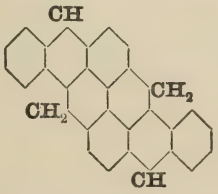
The condensation can be effected in numerous ways, of which the following are the more important:—

(1) By heating the dimethylanthraquinonyl at 350–380° for half an hour.

(2) By fusing it with 30 parts of zinc chloride at 280° for 15 minutes.

(3) By fusing it with 15 parts of caustic alkali and 1 part of anhydrous sodium acetate at 240° for half an hour.

The name pyranthrene is given to this substance in order to indicate its analogy to flavanthrene and indanthrene. Strictly speaking, it is pyranthrone, and pyranthrene is the hydrocarbon which is formed from it by reduction with phosphorus and hydriodic acid, and which has the constitution

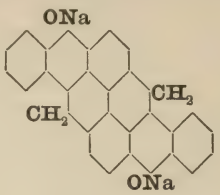


(Pyranthrene).

In this description the name pyranthrene is given to the colouring matter.

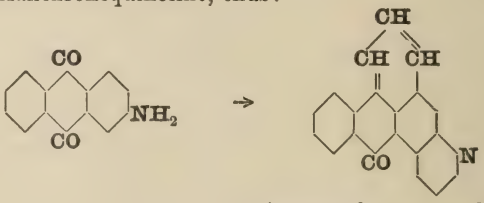
When reduced by alkaline hydrosulphite, pyranthrene yields a purple-red vat in which unmordanted cotton is dyed bright purple. The fibre thus coloured becomes a brilliant orange when exposed to the oxidising action of the air. Unlike flavanthrene and indanthrene, pyranthrene is reduced directly to the

tetrahydro-derivative in the hydrosulphite vat, and it is the sodium compound of this substance which gives the vat its purple-red colour



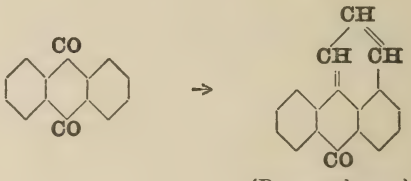
The introduction of halogen atoms into the molecule of pyranthrene changes the shade towards red, and of these dibromopyranthrene (E.P. 12,568[09], A.P. 955,105) is the reddest.

3. *The Benzanthrone Colours.*—During some experiments on the preparation of quinoline derivatives of anthraquinone by the aid of the Skraup reaction, O. Bally (*Ber.*, 1905, xxxviii. 194) found that when 2-aminoanthraquinone is treated with glycerine and sulphuric acid in the absence of an oxidising agent (*Ber.*, 1911, xliv. 1657), two glycerine residues take part in the reaction with the production of benzanthronequinoline, thus:—



(Benzanthronequinoline).

Consequently, it follows that when anthraquinone is treated in the same manner it is converted into the parent substance of this group of colours, viz. benzanthrone



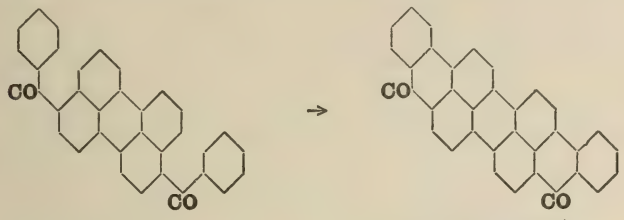
(Benzanthrone).

Benzanthrone can also be prepared by other methods, for example, from anthranol with glycerine and sulphuric acid (Bally and Scholl, *Ber.*, 1911, xliv. 1665), and from phenyl α-naphthyl ketone through the agency of aluminium chloride (E.P. 16,271[10]):

Benzanthrone yields a greenish-yellow vat with alkaline hydrosulphite which contains dihydrobenzanthrone, but the compound is of no importance as a colouring matter. The technically important members of the series are derived from benzanthrone and its derivatives by fusion with potash, and are formed by

the condensation of two molecules of the ketone with loss of four atoms of hydrogen. To this group belong *Indanthrene dark blue* BO (E.P. 16,538[04], A.P. 818,992), and its chloro-derivative *Indanthrene violet* RT (E.P. 22,519[05], 7931[99], A.P. 837,775, 906,367, 1,003,268). *Indanthrene green* B (A.P. 796,393) is prepared by the nitration of Indanthrene dark blue BO. *Indanthrene dark blue* BT is a mixture of Indanthrene dark blue BO and Indanthrene violet RT (*Chem. Zeit.*, 1917, xli. 713).

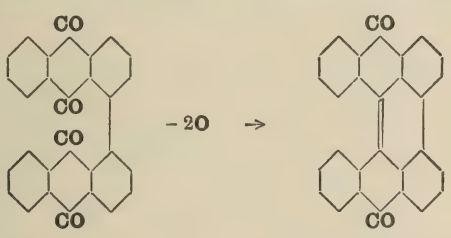
The exact position of the coupling rings in these compounds has not as yet been determined, although it is evident that they must have a structure very similar to that of *Violanthrene* (E.P. 16,528[04], A.P. 818,992, *Ann.*, 1913, cccxcviii. 82), the constitution of which follows from the fact that it is produced when dibenzoyl-1 : 1′-dinaphthyl is treated with aluminium chloride, thus :—



(Violanthrene).

When indanthrene green is chlorinated a deep, fast black is produced.

Helianthrene (*meso*-Benzdianthrone, Scholl and Mansfeld, *Ber.*, 1910, xliii. 1734). The action of copper powder on 1 : 1′ or α-dianthraquinonyl dissolved in concentrated sulphuric acid leads to internal condensation in accordance with the scheme

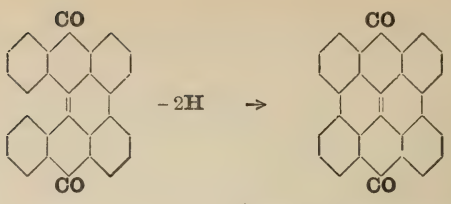


(*meso*-Benzdianthrone).

The compound yields a green vat with alkaline hydrosulphite which contains the alkali salt of the dihydro derivative

and in which unmordanted cotton is dyed green. The dyed fabric changes to yellow on exposure to the air, the shade being deepened by the action of bromine water owing to the bromination of the colouring matter on the fibre.

The action of aluminium chloride on *meso*-benzdianthrone leads to further internal condensation in accordance with the equation

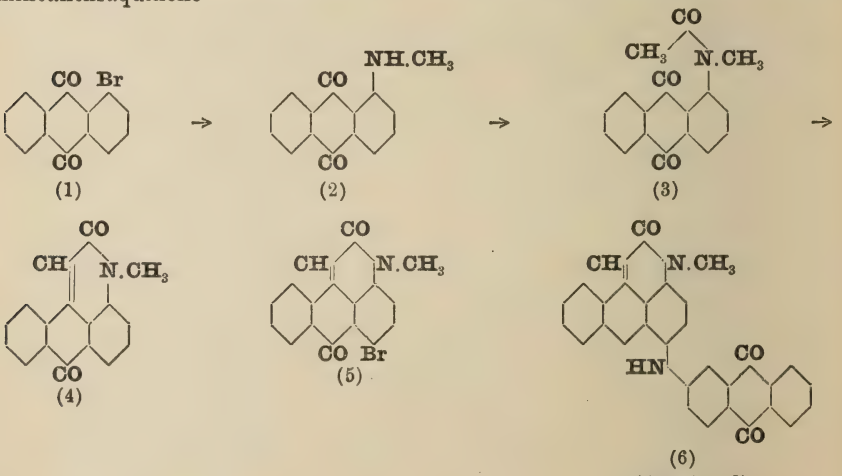


(*meso*-Naphthodianthrone).

meso-Naphthodianthrone forms a flesh-coloured vat with alkaline hydrosulphite in which unmordanted cotton is dyed orange-red. The dyed fibre passes into yellow on exposure to the air.

The above methods of preparation serve to indicate the large number of compounds of this series which are capable of isolation.

4. *Anthraquinoneimides.*—In this class are placed a number of substances which contain two or more anthraquinone residues joined together by one or more imido groups; each pair being attached by one imido group and not by two as in the case of indanthrene. Many important colouring matters belong to this series, as, for example, Algol red, Algol green, Algol blue, and Algol brown, as well as Indanthrene Bordeaux and Indanthrene red. The structure of these substances and their mode of preparation may be illustrated by Algol red, which is prepared in the following way:—1-Bromoanthraquinone (1) is converted into 1-methylaminoanthraquinone (2) by the action of methylamine. This compound is then converted into the acetyl derivative (3), which is transformed into *N*-methylanthraquinonepyridone (4) by the aid of dehydrating agents. The bromination of this compound leads to 4-bromo-*N*-methylanthraquinone-pyridone (5), which is converted into Algol red (6) when condensed with 2-aminoanthraquinone



(Algol red).

The compounds of this group are similar in their properties to the other vat dyes of the series. When reduced by alkaline sodium hydrosulphite they yield coloured vats containing the sodium salt of the dihydro derivative in solution. Cotton dyed in these vats reverts to the colour of the original substance on exposure to the air.

5. *Acyl Derivatives of Aminoanthraquinone.*—Into this class are placed

certain of the simpler acyl derivatives of aminoanthraquinone, which have been found by the Bayer Company of Elberfeld to yield coloured vats in which cotton is substantively dyed the colour of the dihydro derivative; the fibre thus dyed reverts to the colour of the original acyl derivatives on exposure to the air. Algol yellow, Algol rose, and Algol scarlet belong to this group.

Finally, there is a number of colouring matters, prepared from certain derivatives of anthraquinone which, although of great importance technically, have not as yet had any satisfactory structure assigned to them; these substances may be summarised as follows:—

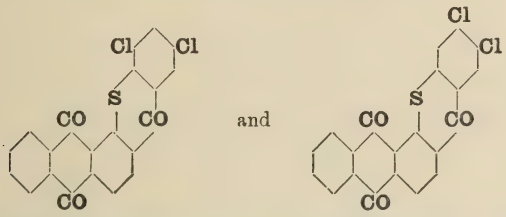
(*a*) From methyleneaminoanthraquinones (from aminoanthraquinones and formaldehyde): Fuscanthrene, etc.

(*b*) From Diaminoanthraquinones on fusion with potash: Melanthrene, Indanthrene maroon and Indanthrene grey.

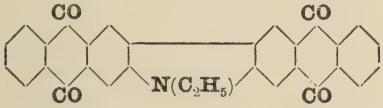
(*c*) From acetyl derivatives of aminoanthraquinones through the agency of phosphorus oxychloride: Indanthrene orange, Indanthrene copper, and Indanthrene olive.

(*d*) From Methylanthraquinone and its derivatives, Cibanon yellow, Cibanon orange, Cibanon brown, Leukol brown, Leukol dark grey, Algol grey, and Helindone brown.

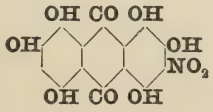
Addendum.—Indanthrene yellow GN [B] and *Indanthrene gold orange* GN [B] (A.P. 1,044,673, 1,044,674, 1,044,675) have the respective formulæ



Hydron yellow G [C], prepared by condensing *N*-ethylcarbazole with phthalic anhydride (E.P. 28,874[11]) has the formula



Alizarine cyanine black G [By], prepared by oxidising β-nitroanthrapurpurine with manganese dioxide is

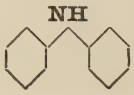


Caledon purple, *Caledon violet*, and *Caledon green* (Solway Dyes Co.), correspond with Indanthrene dark blue BO, Indanthrene violet RT, and Indanthrene green B respectively (see p. 137).

CHAPTER XVIII.

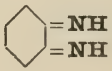
DIPHENYLAMINE DYESTUFFS.

In this class are placed a number of dyestuffs which are all more or less directly related to diphenylamine

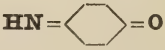


Furthermore, they are all derivatives either of *p*-quinone-di-imide

o-quinone-di-imide

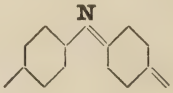
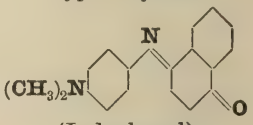
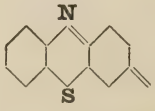
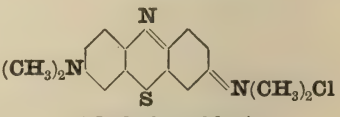
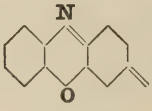
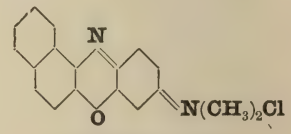


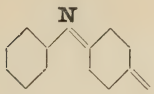
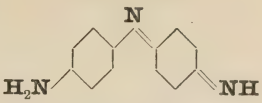
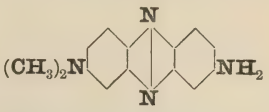
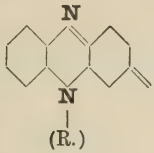
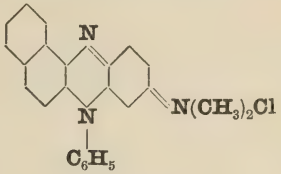
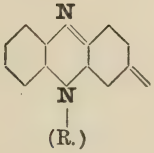
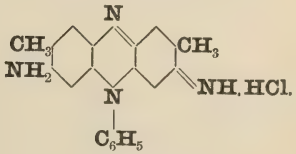
or *p*-quinone-monoimide



the quinone ring in each case being the chromophore of the dyestuff.

This group may be divided into the following classes, which clearly show their relationship to one another:—

Class.	Structure.	Typical Dyestuff.
(1) Indophenols . . .		 (Indophenol).
(2) Thiazines . . .		 (Methylene blue).
(3) Oxazines . . .		 (Meldola's blue).

Class.	Structure.	Typical Dyestuff.
(4) Indamines . . .		 (Phenylene blue (base)).
(5) The azine dyestuffs, comprising:— (*a*) The Eurhodines .		 (Neutral violet (base)).[1]
(*b*) Aposafranines .		 (Neutral blue).[1]
(*c*) Safranines . .		 (Safranine).[1]

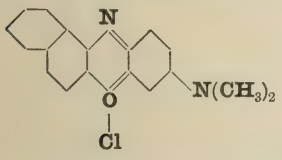
(*d*) The Indulines and Nigrosines.

R. = benzene or naphthalene ring, and sometimes an aliphatic hydrocarbon radicle.

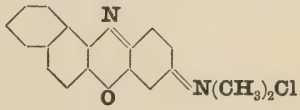
The Aposafranines and the Safranines are placed in separate classes for the sake of convenience. They do not differ in structure.

More recent investigations seem to show that the Oxazines and Thiazines probably possess a formula similar to the Eurhodines and Safranines (see later), in which the salt formation takes place by the passage of dyad oxygen into tetrad oxygen, and of dyad sulphur into tetrad sulphur.

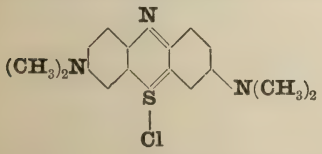
Thus to the hydrochloride of Meldola's blue is given the formula



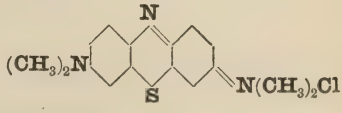
instead of



and to the hydrochloride of Methylene blue, the formula



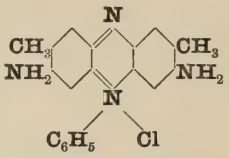
instead of



[1] For the orthoquinone formulæ of these substances, see p. 155.

In this book the older formulæ for these substances have been retained because the authors hold the opinion that it is unreasonable to assume in the present state of our knowledge that salt formation takes place on the feebly basic oxygen or sulphur atom when the strongly basic nitrogen atom is also present in the molecule.

For the same reason they prefer to retain the formula for Safranine given on the previous page instead of

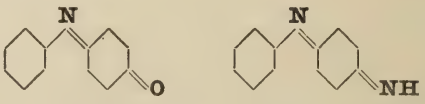


on the ground that the azine nitrogen atom bearing the negative phenyl group would be less basic than the other nitrogen atoms in the molecule.

It must be remembered that owing to the tautomeric changes which these substances undoubtedly undergo in the presence of reagents, experimental evidence respecting their structure is often untrustworthy. (For a general view of this subject see Kehrmann, *Ann.*, 1910, ccclxxii. 337.)

(1) The Indophenols.

As will be seen from the foregoing table, the Indamines and Indophenols are very similar in structure, the only difference being that in the Indophenols, oxygen replaces the group =NH of the Indamines

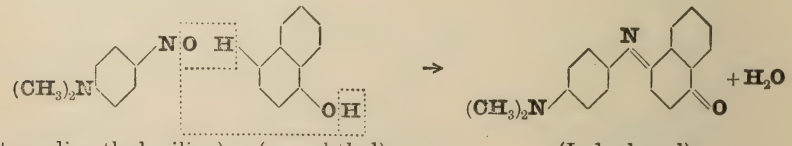


(An Indophenol). (An Indamine).

Owing to the fact that the Indamines are closely related to the Eurhodines and the Safranines, and occur as intermediate products in their preparation, they will be dealt with later together with these dyestuffs.

The Indophenols are made by the oxidation of a mixture of a *p*-diamine and a phenol, or by the interaction of nitrosodimethylaniline with phenols.

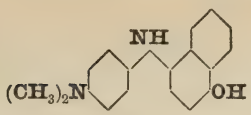
The only technically important Indophenol is prepared from nitroso-dimethylaniline and *α*-naphthol



(nitrosodimethylaniline), (*α*-naphthol), (Indophenol),

and also by the oxidation of a mixture of *p*-amidodimethylaniline and *α*-naphthol (*Köchlin* and *Witt*).

It is a dark brown powder insoluble in water, and is applied to the fibre in precisely the same way as indigo (see p. 325); that is to say, on reduction it yields *Indophenol white*



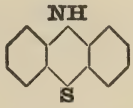
which in alkaline solution possesses affinity for the fibres, upon which it can be reoxidised to the blue on exposure to the air.

(2) Thiazines.

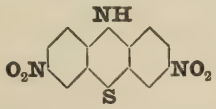
The first dyestuff of this series was discovered by Ch. Lauth in 1876 (*Compt. rend.*, lxxxii. 1441), who prepared a violet dye, which he called Lauth's violet, by oxidising, with ferric chloride, a solution of *p*-phenylenediamine containing sulphuretted hydrogen.

Its constitution and that of other members of this series has been determined by Bernthsen (*Ber.*, 1883, xvi. 1025, 2896; 1884, xvii. 611, 2854, 2857, 2860; and *Ann.*, 1885, ccxxx. 73) in the following way:—

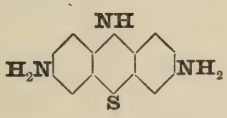
The action of sulphur on diphenylamine yields thiodiphenylamine



which, on nitration, yields a *p*-dinitro-derivative

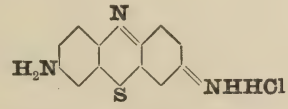


and this in its turn is transformed, on reduction, into di-*p*-amidothiodiphenylamine



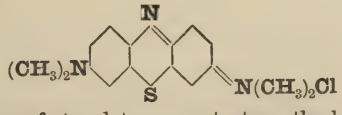
which is the leuco-base of Lauth's violet, yielding this dyestuff on oxidation and conversion into the hydrochloride.

Consequently Lauth's violet has the constitution



It [1] is now of little importance, and has been replaced by the most important member of this series—

Methylene blue B [B]



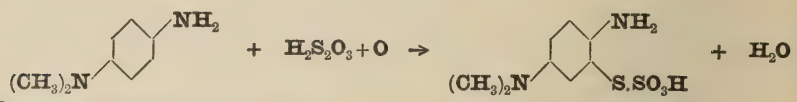
[1] This dyestuff was never manufactured to any extent on the large scale, the small yield of it (scarcely 20 per cent.) rendering its production too costly.

This dyestuff was first prepared by Caro in 1876, who applied Lauth's reaction to *asym*-dimethyl-*p*-phenylenediamine, and who, in conjunction with the Badische Anilin und Soda Fabrik, prepared it technically (E.P. 3751[77]) by oxidising amidodimethylaniline, prepared from nitrosodimethylaniline, in the presence of hydrogen sulphide.

At the present time Methylene blue is produced solely by the "thiosulphate process," which consists in oxidising dimethyl-*p*-phenylenediamine and dimethylaniline in the presence of sodium thiosulphate and zinc chloride.

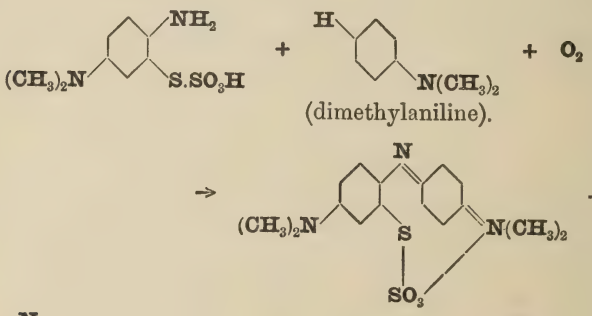
The course of this reaction may be represented by the following equations :—

(1)

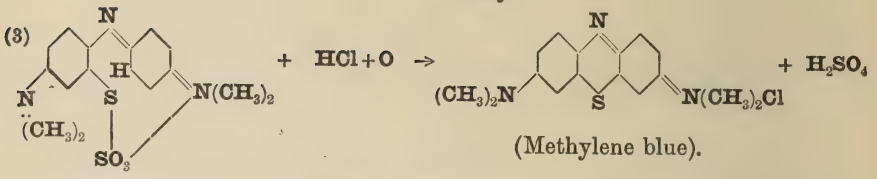


(*asym*-dimethyl-*p*-phenylenediamine). (a thiosulphonic acid).

(2)



(3)

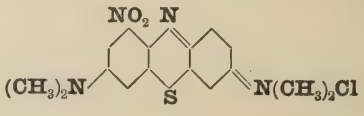


(Methylene blue).

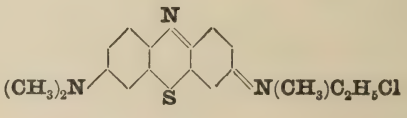
Methylene blue is usually met with in commerce in the form of its zinc chloride double salt, and is a most important dye for cotton, upon which it is fixed by the aid of tannin. It is not well adapted for the dyeing either of silk or wool.

Other dyestuffs of this series are :—

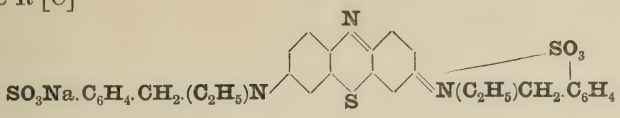
Methylene green [M], from Methylene blue and nitrous acid



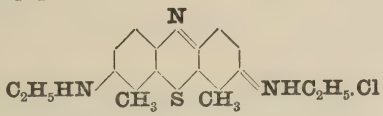
Thionine blue G [M]



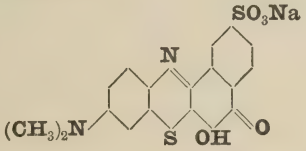
Thiocarmine R [C]



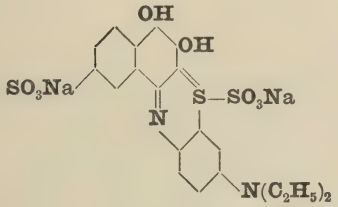
New methylene blue N [C]



Brilliant alizarine blue GR [By]



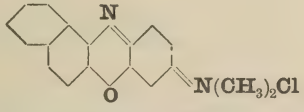
Indochromogen S [S]



(3) Oxazines.

The first dyestuff of this group was discovered by Meldola in 1879, who prepared it by condensing β-naphthol with nitrosodimethylaniline hydrochloride in glacial acetic acid solution.

Its constitution is represented by the formula



(Meldola's blue).

It also occurs in commerce under the names Fast blue, New blue R [C], Cotton blue R [B], etc.

The dyestuff is now formed by using alcohol as a solvent instead of glacial acetic acid, and it is advisable to keep the proportion of β-naphthol and nitrosodimethylaniline—

1 mol. β-naphthol : 2 mols. of the latter.

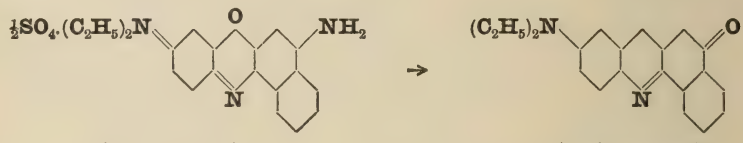
(*Private communication*, R. Meldola.)

It is largely used for the dyeing of tannined cotton.

An important discovery respecting the behaviour of certain colouring matters of this series has been recently made by Lorrain Smith of the Manchester University. This pathologist finds that when microscope sections containing protein matter mixed with neutral fat globules are stained by, for example, Nile blue A (p. 148), the protein matter is coloured in the ordinary way blue, but the fat globules become at the same time deep red. This valuable property of causing differential staining was found to be possessed by other colouring matters of the series, such as New Methylene blue GG, Nile blue BB, and Meldola's blue, although these colours did not exhibit these properties in so marked a manner as Nile blue A.

The cause of this phenomenon has been shown to be as follows (*J.C.S.*, 1907, xci. 324):—

The action of water or of very dilute mineral acid on Nile blue A causes hydrolysis of the amino-group in position (6) and yields the corresponding oxazone



(Nile blue A). (Red oxazone).

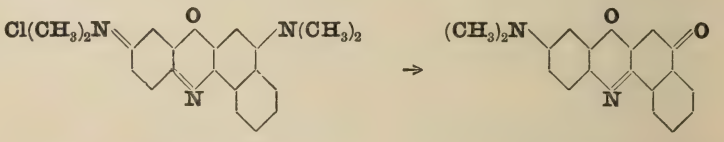
The extent to which this change takes place depends on the length of time during which the acid is allowed to act and on the temperature, but a condition of equilibrium between the salts of the two bases appears to be reached after boiling with water or dilute acid for fifteen minutes.

Both salts are blue, and there is consequently no apparent change in the colour of the dye solution, but the salt of the weaker oxazone base is readily dissociated, and the free red base can be completely extracted by shaking the solution with, for example, xylene, leaving the unchanged Nile blue salt in solution. It therefore follows that when a section is stained in the boiled solution, the protein matter is coloured blue by the unchanged Nile blue present, whereas the neutral fat globules extract the oxazone base from the solution of its salt, and are consequently stained red.

This property can be further illustrated by dyeing wool in the boiled solution of the colouring matter, for the blue-dyed fibre will become markedly purple when washed with water, owing to the formation of the red oxazone on the fibre.

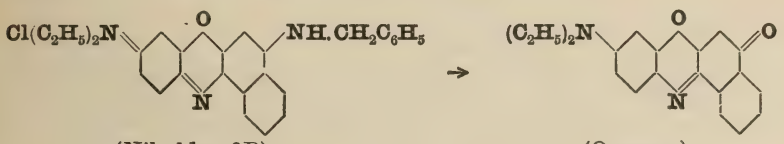
The reason why Nile blue A exhibits this property to a greater degree than any other member of the series is because of the presence of the free amino-group in position (6).

When the hydrogen atoms of this group are substituted, the formation of the oxazone depends on the nature of the substituting groups. Thus New Methylene blue GG is transformed into the oxazone almost as readily as Nile blue A.



(New Methylene blue GG). (Oxazone).

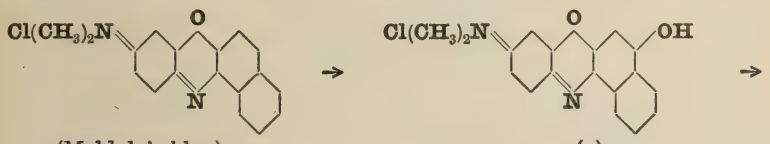
and this colouring matter can be used for differential staining. On the other hand, Nile blue 2B (p. 148) is unaffected by boiling water, but is converted into the oxazone on prolonged boiling with dilute mineral acids.



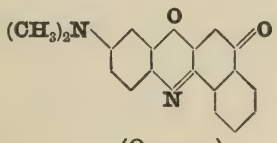
(Nile blue 2B). (Oxazone).

The remarkably reactive character of the position (6) in compounds of this type is also illustrated by the behaviour of Meldola's blue, for this colouring matter also produces differential staining after having been boiled with dilute mineral acid.

Experiment shows that in this case the oxazone is produced by the oxidation of the hydrogen atom in position (6) in accordance with the scheme



(Meldola's blue). (*a*)

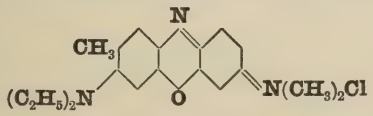


(Oxazone).

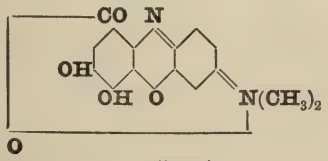
From the fact that the salts of the oxazones are blue, it is probable that they possess a structure represented by formula (*a*), and that rearrangement ensues when the salt is transformed into the red oxazone. This assumption is strongly supported by the fact that wool is dyed blue in a bath of the oxazone containing sufficient acid to prevent dissociation, and that when the fibre thus dyed is washed with water it becomes red.

Other dyestuffs of this series are :—

Capri blue GON [By]—nitrosodimethylaniline + diethyl-*m*-amidocresol

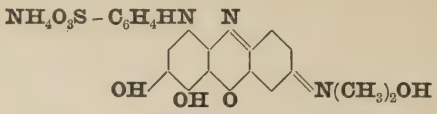


Gallocyanine DH [DH]—nitrosodimethylaniline + gallic acid



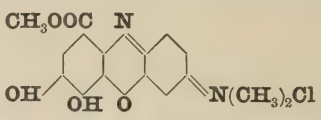
(base).

Delphin blue [S]—Gallocyanine + aniline and sulphonation

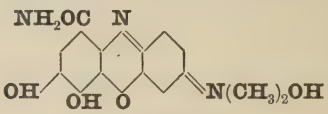


(ammonium salt).

Prune pure [S]—nitrosodimethylaniline + methyl ester of gallic acid

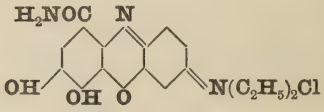


Gallamine blue [By]—nitrosodimethylaniline + gallaminic acid (gallamide)

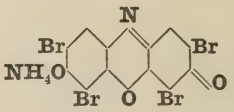


(base).

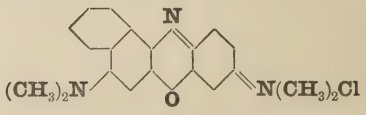
Coreïne RR [DH]—nitrosodiethylaniline + gallamide



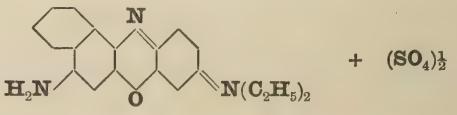
Iris blue [B]—nitrosoresorcinol + resorcinol and bromination



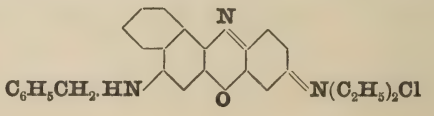
New methylene blue GG [C] — dimethylamine + Meldola's blue and oxidation



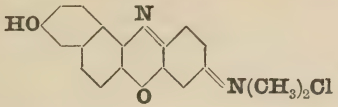
Nile blue A [B]—nitrosodiethyl-*m*-amidophenol + α-naphthylamine



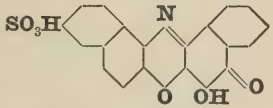
Nile blue 2B [B]—nitrosodiethyl-*m*-amidophenol + benzyl-α-naphthylamine



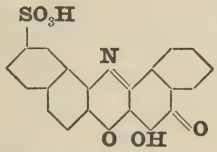
Muscarine [DH]—nitrosodimethylaniline + 2 : 7-dioxynaphthalene



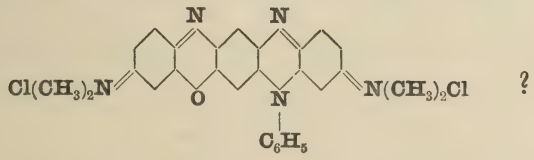
Alizarine green G [D] — β-naphthoquinone sulphonic acid + 1-amido-2-naphthol-6-sulphonic acid



Alizarine green B [D] — β-naphthoquinone sulphonic acid + 2-amido-1-naphthol-4-sulphonic acid



Fast black [L] —nitrosodimethylaniline + *m*-oxydiphenylamine

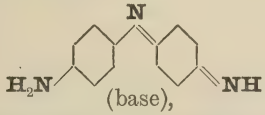


(4) Indamines.

The dyestuffs of this group belong to the oldest of the artificial colouring matters, some of them having been formed by Runge and Perkin in their experiments on the oxidation of aniline.

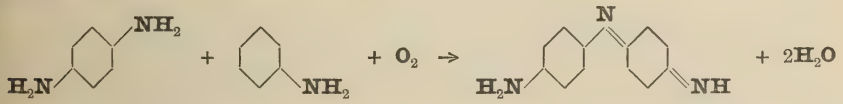
They are mainly interesting as intermediate products in the manufacture of the Eurhodines and Safranines.

The simplest Indamine is *Phenylene blue*

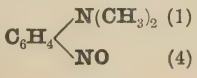


(base),

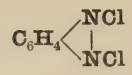
which can be prepared by the oxidation of a mixture of *p*-phenylenediamine and aniline



Indamines can also be prepared by replacing the *p*-phenylenediamine in the above reaction by such bodies as nitrosodimethylaniline



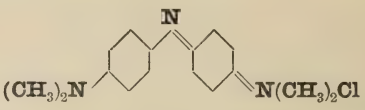
and dichlorquinonimide



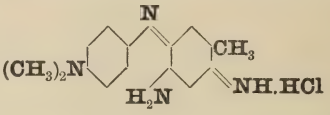
which yield *p*-diamines on reduction.

The dyestuffs of this group are not of any technical importance. Two, however, possess theoretical interest owing to their close relationship to the Eurhodines and Safranines.

Bindschedler's green—dimethyl-*p*-phenylenediamine + dimethylaniline

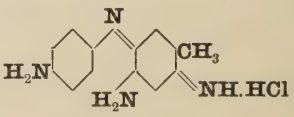


and *Toluylene blue* (Witt)—dimethyl-*p*-phenylenediamine + *m*-toluylenediamine



which is of considerable theoretical importance, since, on heating with water, it passes into the Eurhodine, Neutral red.

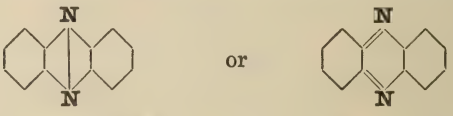
Similarly, *p*-phenylenediamine and *m*-toluylenediamine yield the Indamine



which, on boiling with water, gives the Eurhodine, Toluylene red (see below).

(5) The Azine Group.

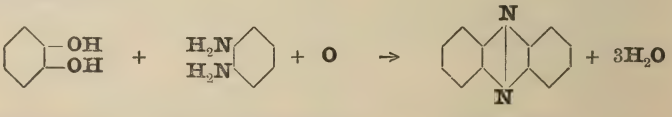
The Azine dyestuffs may be regarded as derivatives of phenazine



and comprise (*a*) the Eurhodines, (*b*) the Aposafranines, (*c*) the Safranines, (*d*) the Indulines and Nigrosines.

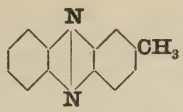
(*a*) **The Eurhodines.**—These dyestuffs are amido-derivatives of phenazine, and their constitution has been determined in the following way:—

Phenazine was obtained by Merz and Ris by condensing pyrocatechol with *o*-phenylenediamine



(pyrocatechol). (*o*-phenylenediamine). (phenazine).

In the same way they prepared methylphenazine

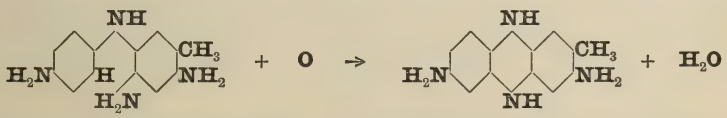


from pyrocatechol and *o*-toluylenediamine.

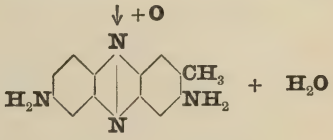
Now the Toluylene red mentioned above was found by Bernthsen and Schweitzer (*Ann.*, 1886, ccxxxvi. 332) to give the same methylphenazine on eliminating its two amido-groups.

It must therefore be a diamidomethylphenazine of the formula

and its formation from the Indamine can be represented by the following scheme:—

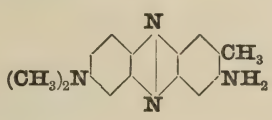


(The Indamine (leuco-compound)). (Toluylene red (leuco-compound)).



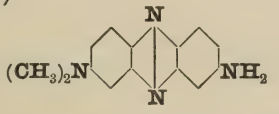
(Toluylene red (base)).

In the same way the *Neutral red* [C], mentioned above as having been prepared from Toluylene blue, has the formula (base)



The only other Eurhodine of importance is *Neutral violet* [C], prepared by the oxidation of a mixture of *p*-amidodimethylaniline and *m*-phenylenediamine.

It has the formula (base)



The Aposafranines, Safranines, and Indulines differ from the Eurhodines in that one of the nitrogen atoms of the phenazine molecule is combined with another benzene or naphthalene ring.

The Aposafranines are monoamido-derivatives or monohydroxy-derivatives. The Safranines are diamido- and the Indulines tri- or tetraamido-derivatives of the phenazine so substituted.

Constitution and History of the Aposafranines and Safranines.

Substances belonging to the group of the Safranines are among the oldest of the coal-tar colouring matters, since Mauveïne, the first artificial dyestuff prepared (Perkin, *Proc. R.S.*, xxxv. 717), belongs to this group.

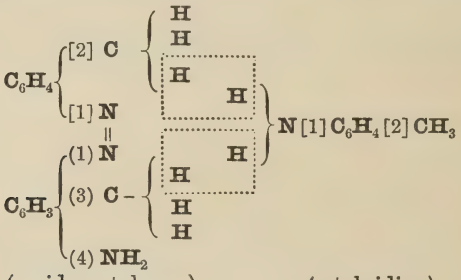
From the mother liquors from Mauveïne, Perkin (*Chem. News*, 1861, iii. 348) isolated a red dyestuff, to which he gave the name Pink (*Chem. News*, 1869, xix. 181), and which he suggested (*ibid.*, 1870, xxii. 80) might be identical with Safranine.

The first technical production of Safranine under this name was carried out under the French patents[1] of Felix Duprey in 1865, but without success; and it was not until 1868 that Lotz, of Basle, produced it in any quantity under the name of Safflorsurrogat.

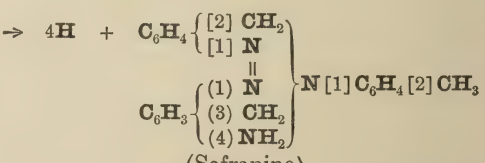
The first technical production of Safranine in Germany was carried out by Caro, who at first employed the Duprey method, but subsequently adopted that discovered by Nietzki, which consisted in heating *p*-toluidine-azo-*o*-toluidine and *o*-toluidine-azo-*o*-toluidine in acetic acid solution together with a small quantity of nitric acid, on the water-bath.

In 1877 Witt (*Ber.*, x. 874) published a constitutional formula for Safranine, based upon the fact that it could be prepared by heating amidoazotoluene with *o*-toluidine in alcoholic solution.

The equation representing the reaction he gave as follows:—



(amidoazotoluene). (*o*-toluidine).



(Safranine).

And a similar azo-formula for this substance was proposed in 1879 by Perkin (*J.C.S.*, 1879, xxxv. 717).

The incorrectness of these formulæ was shown by the discovery by Witt in 1878 of phenosafranine, which he prepared by the oxidation of a mixture of *p*-phenylenediamine and aniline; and it was subsequently found that the Safranines are formed by the joint oxidation of 1 mol. of a *p*-diamine with 2 mols. of a monamine.

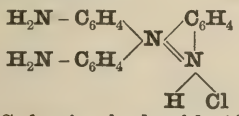
The first insight into the true constitution of the Safranines was afforded by Nietzki, who prepared a Safranine by the oxidation of equal molecules of diethyl-*p*-phenylenediamine and aniline, whereby the existence in Safranine

[1] The methods consisted in (1) oxidising Mauveïne with barium peroxide; (2) heating Aniline in acetic acid solution with lead nitrate.

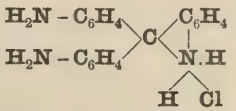
of two monoamine radicles with their benzene rings attached to nitrogen became probable.

Nietzki also prepared a tetraethyl safranine which supplied further evidence of the presence of two amido-groups in the safranine molecule.

He then gave this dyestuff the following formula, in which a relationship to *p*-rosaniline is indicated :—

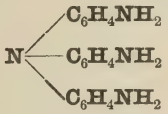


(Safranine hydrochloride).



(Rosaniline hydrochloride).

Leuco-safranine (prepared from Safranine on reduction) he considered to be triamidotriphenylamine

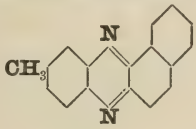


The incorrectness of these formulæ soon became apparent, however, when it was found that phenosafranine had the empirical formula $C_{18}H_{14}N_4HCl$, or two atoms of hydrogen less than that assumed by Nietzki.

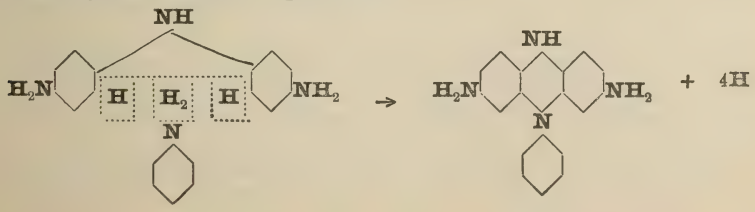
The next step in the solution of this problem was taken by Witt (*Ber.*, 1885, xviii. 1119), who found that by the condensation of amidoazotoluene (from *p*-toluidine) with α-naphthylamine hydrochloride a yellow compound, closely allied to the Safranines, was formed, and not a complicated Induline dyestuff, such as was produced from other primary amines.

He further found that similar compounds were also formed when other amidoazo-compounds containing the amido-group in the *ortho*-position to the azo-group were heated with α-naphthylamine.

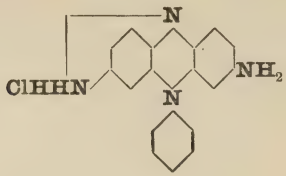
The compounds so produced Witt called Eurhodines, and for the compound formed from amidoazotoluene and α-naphthylamine he proposed the formula



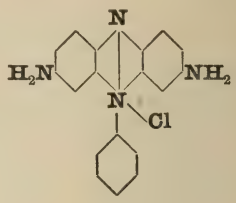
About this time the work of Merz and Ris on phenazine, already referred to, was published, and therefrom resulted the elucidation of the constitution of Toluylene red by Bernthsen and Schweitzer. These facts, together with the discovery of the close relationship between the Indamines and Safranine on the one hand, and on the other the analogy between Toluylene red and Safranine, led Bernthsen (*Ber.*, 1886, xix. 2691) to the assumption that the leuco-compound of phenosafranine was formed by the interaction of equal molecules of *p*-diamidodiphenylamine and aniline, and that its formation could be represented by the following equation :—



For the dyestuff which is prepared by the oxidation of the leuco-base and subsequent conversion into the salt, he proposed two formulæ :—



and

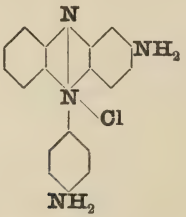


I. II.

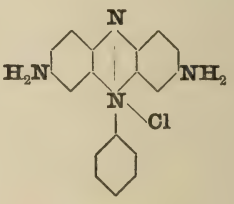
Formula I. does not give the two amido-groups which are assumed to be present in Safranine, and therefore formula II. alone suffices to explain its constitution.

Against this formula Nietzki (*Ber.*, 1886, xix. 3164) argued that it did not explain the existence of two isomeric dimethylsafranines, which he had prepared, and found to be different by a close examination of their crystalline form and solubility.

Bernthsen (*Ber.*, 1887, xx. 179) examined these dimethylsafranines, and also came to the conclusion that they were different. He therefore, with Nietzki, adopted an asymmetrical formula proposed by Witt (*Ber.*, 1886, xix. 3121) :—

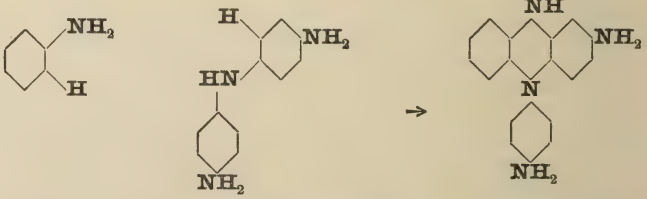


(Witt's formula).



(Bernthsen's formula).

The formation of the Safranine of this formula from di-*p*-amidodiphenylamine and aniline, Witt explained by the following equation :—



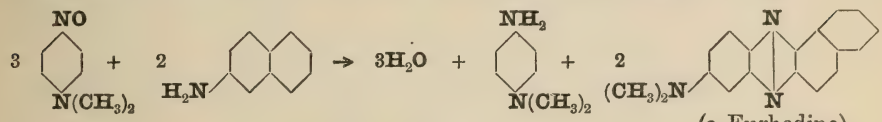
(aniline). (*p*-diamidodiphenylamine). (leucosafranine).

For some time the asymmetric formula was accepted as correct, until Körner and Schraube showed that it had been founded upon an error, and that the two isomeric dimethylsafranines of Nietzki were in reality identical.

This led to the readoption of the symmetrical formula, which has since been verified by a number of experimental facts.

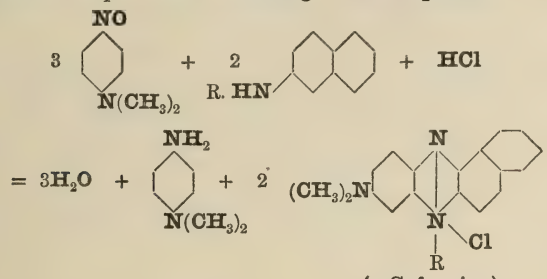
In 1888 Witt (*Ber.*, xxi. 719) published some experiments which clearly indicate the close relationship between the Eurhodines and the Safranines.

If nitrosodimethylaniline is condensed with β-naphthylamine, dimethylphenylnaphtheurhodine is produced according to the equation



(a Eurhodine).

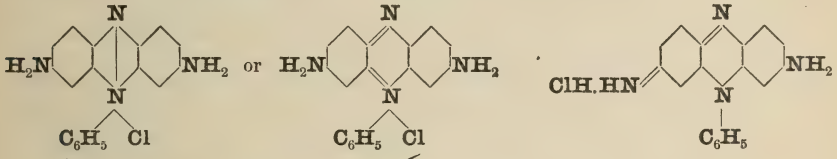
If, however, the β-naphthylamine is replaced by a secondary base derived from it, a Safranine is produced according to the equation



(a Safranine).

Other investigations on the constitution of Safranine have more recently been published by Kehrmann and Messinger (*Ber.*, 1891, xxiv. 584, 2167), Kehrmann (*ibid.*, 1894, xxvii. 3349), Jaubert (*ibid.*, 1895, xxviii. 270, 508, 1581; 1896, xxix. 414), Nietzki (*ibid.*, 1895, xxviii. 1354; 1896, xxix. 1442), O. Fischer and Hepp (*ibid.*, 1893, xxvi. 1195, 1655; 1895, xxviii. 2283; 1896, xxix. 361; *Ann.*, 1895, cclxxxvi. 211), and O. Fischer (*Ber.*, 1896, xxix. 1870; see also Kehrmann, *Ann.*, 1910, ccclxxii. 337).

The main object of these researches was to determine which of the two following formulæ represented the constitution of Safranine chloride:—

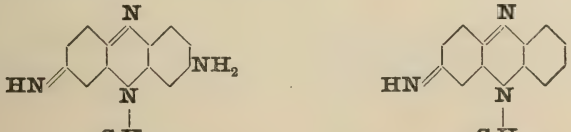


I. II.

One of the chief points which had to be explained was the following:—

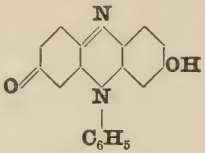
Safranine readily yields a diazo-salt with nitrous acid, which, on boiling with alcohol, gives Aposafranine, a substance which does not react with nitrous acid under ordinary conditions, and therefore presumably does not contain a primary amido-group.

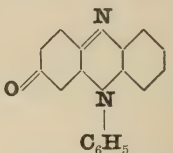
This behaviour can only be explained on the assumption that formula II. represents the constitution of Safranine



(Safranine). (Aposafranine).

Similar behaviour is exhibited by the corresponding hydroxyl derivatives Aposafranole and Safranole

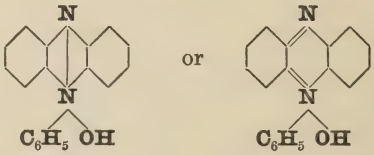

(Safranole).


(Aposafranole).

In Safranole only one hydroxyl group can be detected, and in Aposafranole none at all.

O. Fischer and Hepp, however, prepared certain chlorine derivatives from Aposafranole and Safranole, the formation of which can only be explained on the assumption that these substances have the orthoquinoid structure represented by formula I. Kehrmann also showed that Aposafranine could be diazotised by dissolving it in concentrated sulphuric acid, and treating the green solution thus formed with nitrous acid.

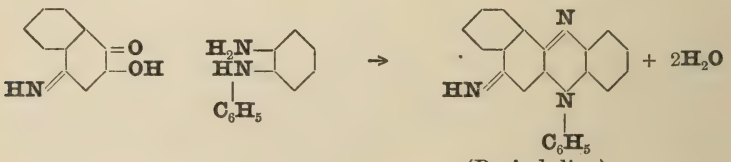
On boiling this diazo-salt with alcohol he obtained an azonium base—phenylphenazonium



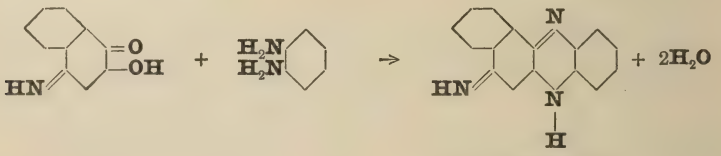
This behaviour of Aposafranine seems to indicate that at any rate in concentrated sulphuric acid solution it contains a primary amido-group, and that therefore, under these conditions, it possesses an orthoquinone structure; and these considerations, taken in conjunction with those already mentioned, would seem to show that Safranine can react either as a *para-* or as an *ortho*-quinone derivative, according to the nature of the reaction involved.

In the case of diamidoeurhodines, both amido-groups are readily diazotisable, and therefore there is no reason to assume a *para*quinone structure; but, as Kehrmann has shown by the following experiments, they also appear to react in two forms.

Rosinduline is formed from phenyl-*o*-phenylenediamine and oxynaphthoquinoneimide

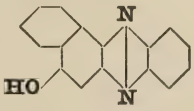

(Rosinduline).

If the phenyl-*o*-phenylenediamine is replaced by *o*-phenylenediamine, a Eurhodine is formed

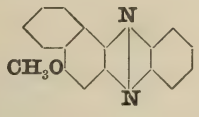

(a Eurhodine).

From these experiments, therefore, the Eurhodines would appear to be *p*-quinone derivatives.

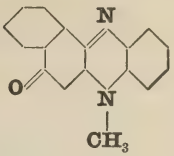
Kehrmann and Messinger attempted to decide this question by methylating a Eurhodole of the formula



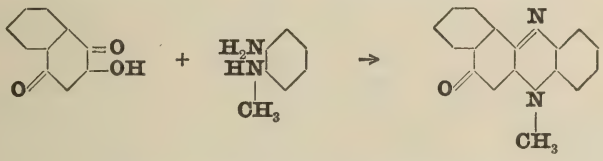
The methyl ether formed would then have either the formula



or



and, if the latter, it would be identical with the Eurhodine prepared by the condensation of oxynaphthoquinone with methyl-*p*-phenylenediamine



Kehrmann and Messinger found that two methyl ethers are formed by the methylation of the above eurhodole, and one of them is identical with the methyleurhodole obtained by the condensation given above.

Therefore the Eurhodines, like the Safranines, appear to be desmotropic substances.

(*b*) The Aposafranines.

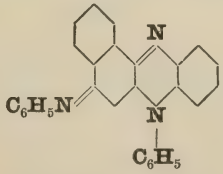
These dyestuffs are, as already mentioned, monoamido- and monohydroxy-derivatives of phenyl- or naphthylphenazine.

Many of them are prepared by melting together a mixture of an amidoazo-compound with a primary base and its salt, and an explanation of this process will be given under the head of the Indulines.

The two following dyestuffs belong to this group :—

Azocarmine G [B] is prepared by fusing aniline-azo-α-naphthylamine + aniline + aniline hydrochloride and subsequently sulphonating with fuming sulphuric acid.

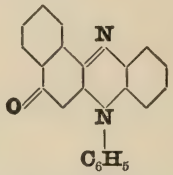
It is the sodium salt of phenylrosinduline disulphonic acid



(Phenylrosinduline).

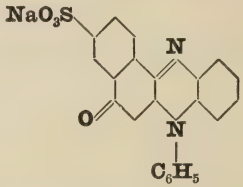
Azocarmine B [B] is the sodium salt of phenylrosinduline trisulphonic acid, made by the further treatment of phenylrosinduline with fuming sulphuric acid.

On treating this trisulphonic acid with water at 160–180°, it is converted into *Rosinduline* 2G [K], which is the sodium salt of a rosindone monosulphonic acid



(Rosindone).

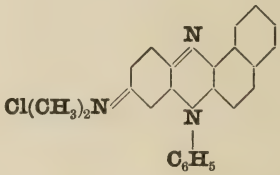
Another sulphonic acid (sodium salt), namely, *Rosinduline* G [K]



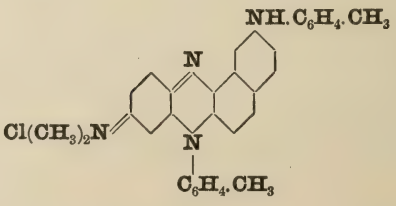
is prepared by heating phenylrosinduline-6-(naph.)-monosulphonic acid with water under pressure.

These dyestuffs are important acid wool dyes.

Neutral blue [*C*]—nitrosodimethylaniline + phenyl-β-naphthylamine—is



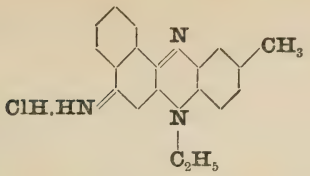
and its derivative, *Basle blue* R [DH] — nitrosodimethylaniline + 2 : 7-ditolyl naphthylenediamine



They are important tannin cotton dyes.

The sulphonic acid (sodium salt) made by the sulphonation of this dyestuff is known as *Basle blue* S [DH].

To this group also belongs *Induline scarlet* [B]



made by melting the azo-derivative of monoethyl-*p*-toluidine with α-naphthyl amine hydrochloride.

(*c*) The Safranines.

These dyestuffs are the diamido-derivatives of phenyl- or naphthylphenazine They can be prepared :—

(1) By the oxidation of an Indamine (or of the basic mixture that would yield an Indamine) and a monamine; that is to say, by the oxidation of 2 mols. of a monamine and 1 mol. of a *para*diamine under the following conditions:

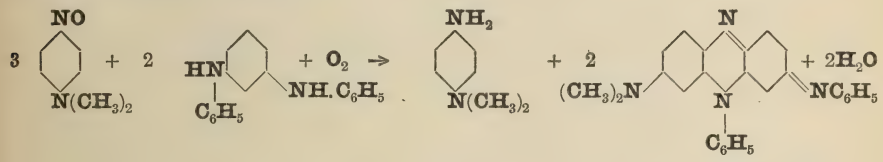
(*a*) Only one amido-group of the *p*-diamine may be substituted.

(*b*) One molecule of the monamine must have its *para*-position free.

(*c*) The other molecule of the monamine must be primary. The preparation of Safranine (p. 291) is an example of this method.

(2) By the interaction of nitrosodialkylaniline and secondary bases derived from *m*-phenylenediamine.

An example of this method is *Indazine* M [C] — nitrosodimethylaniline + diphenyl-*m*-phenylenediamine

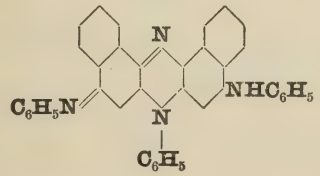


(Indazine (base)),

a blue tannined cotton dyestuff.

(3) By melting certain amidoazo-compounds with primary bases (see p. 164).

An example of this method is *Milling blue* [K] (Naphthyl blue)—aniline-azo-α-naphthylamine + α-naphthylamine HCl + aniline

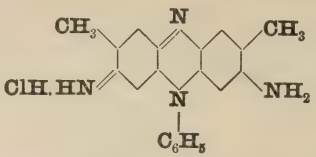


(Sulphonated.)

This reaction can be explained by assuming the decomposition of the amidoazo-compound into bases suitable for the production of Safranines.

Milling blue is a wool dye, and is affixed to the fibre by the aid of chromium salts.

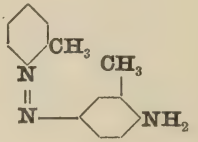
The most important member of this group is *Safranine* T [B]



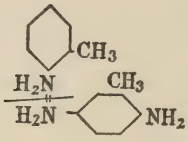
It is made by the oxidation of equal molecules of *p*-toluylenediamine and *o*-toluidine to the Indamine, which is converted into the Safranine by oxidation with aniline.

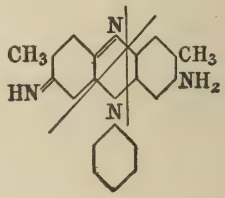
It is also sometimes made from an aniline rich in *o*-toluidine (aniline oil for Safranine), and from the basic mixture known as *échappés*, which distils over during the manufacture of Magenta.

This basic mixture, which contains large quantities of *o*-toluidine, on treatment with nitrous acid forms the azo-compound



which is first reduced to form *o*-toluidine and *p*-toluylenediamine, and then these two bases are oxidised with aniline to form Safranine





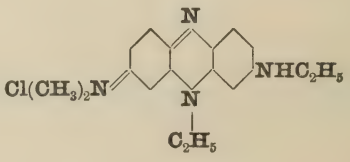
(Safranine (base)).

Safranine is a basic dyestuff well adapted for dyeing cotton red on a tannin mordant. It gives characteristic colorations with strong sulphuric acid, dissolving to form a green solution, which, on gradual dilution, passes through blue and violet to red.

When treated with nitrous acid it yields a diazo-salt, which on combining with β-naphthol gives *Indoine blue* R [B], an important dyestuff, dyeing both unmordanted and tannined cotton fast indigo shades of blue.

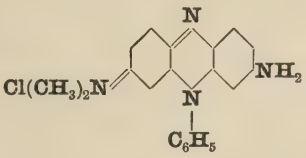
Other dyestuffs of this group are:—

Fast neutral violet B [C] — nitrosodimethylaniline + diethyl-*m*-phenylenediamine



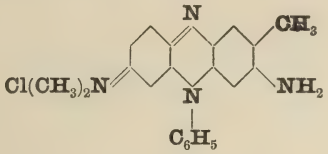
dyeing tannined cotton a fast violet shade.

Methylene violet RRA, 3RA [M]—oxidation of dimethyl-*p*-phenylenediamine + aniline



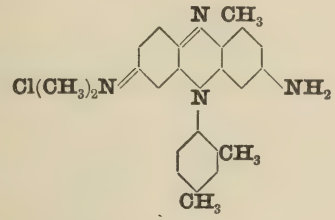
dyeing tannined cotton red-violet.

Safranine MN—oxidation of dimethyl-*p*-phenylenediamine + aniline + *o*- or *p*-toluidine; for example :—



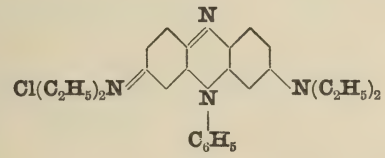
also producing red-violet shades on tannined cotton.

Girofle [DH]—nitrosodimethylaniline + a mixture of *m*- and *p*-xylidine; for example :—



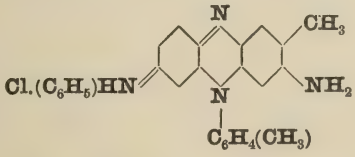
dyeing tannined cotton red-violet.

Amethyst violet [K]—oxidation of diethyl-*p*-phenylenediamine + diethylaniline + aniline



dyeing silk violet with red fluorescence.

Mauveïne—oxidation of aniline containing toluidine; for example :—



This dyestuff is most interesting from an historical point of view, since it was the first artificial dyestuff prepared.

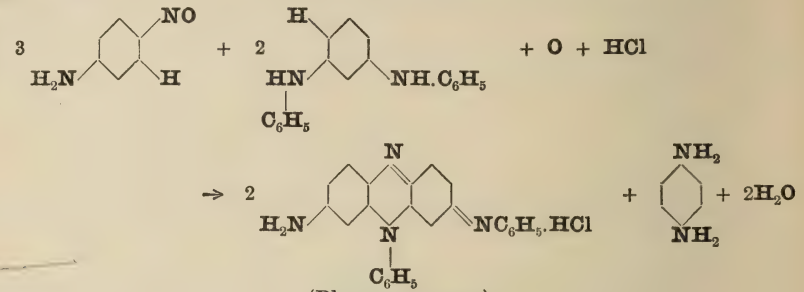
In 1856 Perkin (*Zeitschr. f. Ch.*, 1861, 700) attempted to prepare quinine by the oxidation of allyltoluidine

$$2C_6H_4(CH_3)NH.C_3H_5 + 2O_2 \rightarrow C_{20}H_{24}N_2O_3 + H_2O$$

but obtained instead a dark-coloured precipitate. A similar substance was also obtained by the action of potassium bichromate on aniline sulphate, which, on closer investigation, yielded a violet dyestuff, which Perkin patented in England on 26th August 1856, and proceeded to manufacture on the large scale, under the name of Mauve.

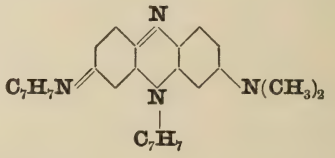
Mauveïne is now little used. Until quite recently it was employed for printing the mauve penny postage stamps of the last century.

The constitution of Mauveïne is shown by the synthesis of phenomauveïne from nitrosoaniline and diphenyl-*m*-phenylenediamine (*Fischer* and *Hepp*)



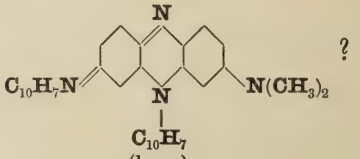
(Phenomauveïne).

Metaphenylene blue B [C]—nitrosodimethylaniline + di-*o*-tolyl-*m*-phenylenediamine



dyes tannined cotton Indigo blue.

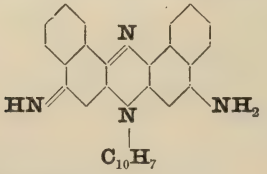
Naphthazine blue [D] [M] — nitrosodimethylaniline + β-dinaphthyl - *m*-phenylenediamine disulphonic acid



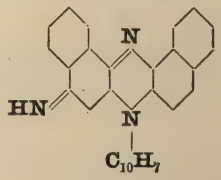
(base)

is a blue acid wool dye.

Magdala red—α-amidoazonaphthalene + α-naphthylamine ; *bases* :—



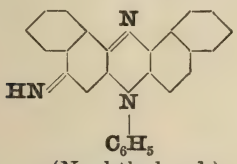
and



is used in silk dyeing.

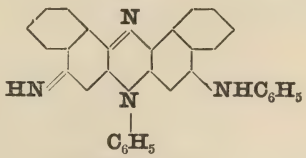
Naphthyl red [K] and Naphthyl blue [K] are two silk dyestuffs which are sodium salts of sulphonated rosindulines similar to Naphthyl blue described above.

They are the sulphonic acids of the bases



(Naphthyl red.)

and



(Naphthyl violet.)

(*d*) The Indulines and Nigrosines.

Under the names Induline, Fast blue, Nigrosine, Bengaline, etc., a group of blue, violet, grey, and black dyestuffs have been known almost from the commencement of the coal-tar industry.

Some are insoluble in water, and these are hydrochlorides or sulphates of the Induline bases; others are soluble, and are the sodium salts of the sulphonic acids made by the sulphonation of these bases.

In general those dyestuffs which are prepared by Caro's method, namely, by heating a mixture of an azo-compound with aniline and aniline hydrochloride, are termed Indulines.

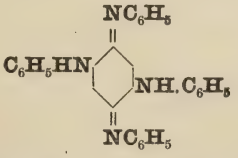
The term Nigrosine is, at the present time, applied to those dyestuffs which are prepared from nitrobenzene or nitrophenol.

Indulines from amidoazobenzene.—The first Induline was prepared by Dale and Caro (Engl. Pat. 3307, 1863) by heating aniline hydrochloride with sodium nitrite, and was manufactured under this name by Roberts, Dale & Co., of Manchester, in 1864.

It soon became apparent that this dyestuff was in reality formed by the interaction of aniline hydrochloride and amidoazobenzene formed from the aniline hydrochloride and sodium nitrite, and its mode of production was scientifically investigated by Martius and Griess (*Zeitschr. f. Chem.*, 1866, 136) and A. W. Hofmann and Geyger (*Ber.*, 1872, v. 472). These chemists found that on heating equal molecules of amidoazobenzene and aniline hydrochloride together with alcohol, in a sealed tube at 160°, the simplest Induline (Azodiphenyl blue), $C_{18}H_{15}N_3.HCl$, was formed.

Azodiphenyl blue was then manufactured on the large scale by heating together amidoazobenzene and aniline hydrochloride in a solution of aniline.

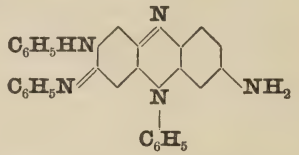
The nature of this reaction was further investigated by Witt and Thomas (*J.C.S.*, 1883, i. 112; *Ber.*, 1883, xvi. 1102), who found that the first product, formed by heating the mixture at 100°, was azophenine (dianilidoquinonedianilide)



a substance previously prepared by Kimich (*Ber.*, 1875, viii. 1028).

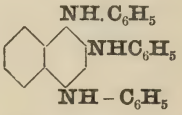
On heating the mixture at 130° this product disappears, being converted into Induline B (Azodiphenyl blue) and Induline 3B—$C_{30}H_{23}N_5.HCl$—and under certain conditions defined by Witt and Thomas (E.P. 3307[63]), a much bluer Induline—Induline 6B—is formed.

The constitution of the base of Induline 3B has been determined by Fischer and Hepp (see next paragraph) as

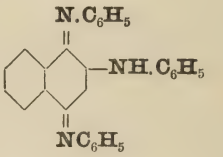


The mode of formation of dyestuffs from amidoazo-compounds.—O. Fischer and Hepp, *Ann.*, 1890, cclvi. 233; 1891, cclxii. 237; 1891, cclxvi. 256; 1893, cclxxii. 306; 1895, cclxxxvi. 187; *Ber.*, 1887, xx. 2479; 1888, xxi. 676, 2617; 1890, xxiii. 838; 1892, xxv. 2731; 1893, xxvi. 1655; 1895, xxviii. 2289; 1896, xxix. 361.

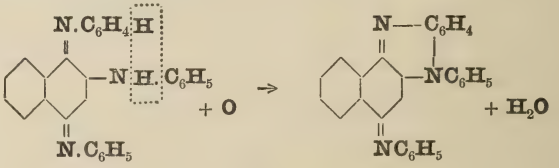
By the interaction of the hydrochloride of 4-nitrosoethyl-α-naphthylamine and aniline in acetic acid solution, there is formed 1 : 2 : 4-trianilidonaphthalene



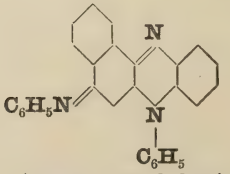
This substance, on oxidation with HgO in benzene solution, is converted first into 2-anilidonaphthoquinone-1 : 4-dianil



and then into phenylrosinduline (Azocarmine G base).



or



(Phenylrosinduline).

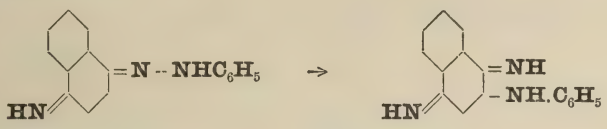
The same dyestuff is also formed (see p. 157) by melting aniline-azo-α-naphthylamine with aniline and aniline hydrochloride.

This formation can be explained in the following manner:—

(1) The amidoazo-compound reacts in its hydrazone form

(azo-form). (hydrazone form).

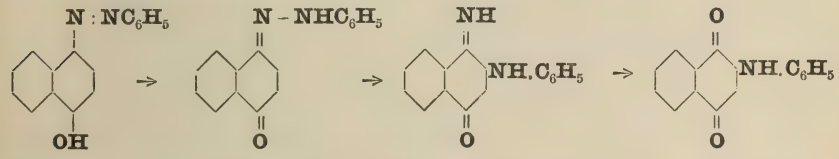
(2) An interchange in positions between a hydrogen of the ring and the anilido-group takes place



(hydrazone form). (anilidonaphthoquinonediimide).

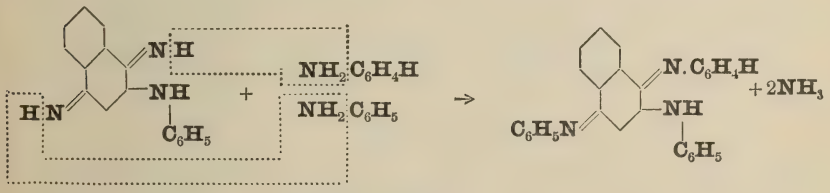
Other instances of a molecular transformation of this kind are known.

Thus, benzene-azo-α-naphthol, on heating for eight hours with glacial acetic acid, is converted into 2-anilidonaphthoquinone together with a small quantity of 2-anilidonaphthoquinone-1-imide



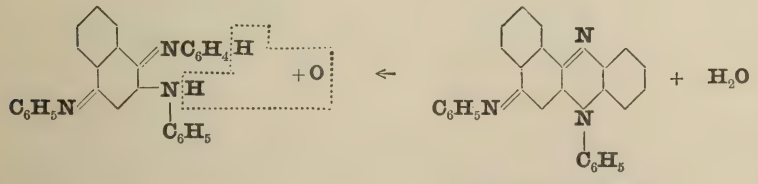
benzene-azo-α-naphthol (azo-form). (hydrazone form). (2-anilidonaphthoquinone-1-imide). (2-anilidonaphtho-quinone).

(3) The formation of the phenylrosinduline then takes place as follows:—



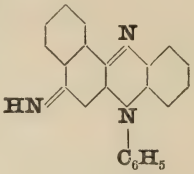
(2 mols. aniline),

and



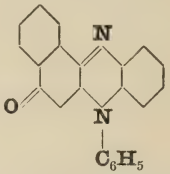
(Phenylrosinduline).

If the above method of forming phenylrosinduline be modified by heating benzene-azo-α-naphthylamine with aniline and alcohol under pressure, the simplest rosinduline of the formula



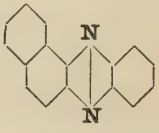
(Rosinduline),

is formed; and when this is heated with concentrated hydrochloric acid under pressure, the corresponding rosindone is produced



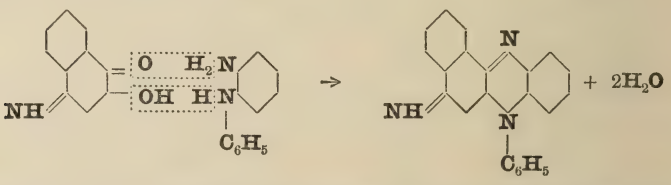
(Rosindone (see *Rosinduline* 2G)),

and the substance, on distillation with zinc dust, yields α-naphthophenazine

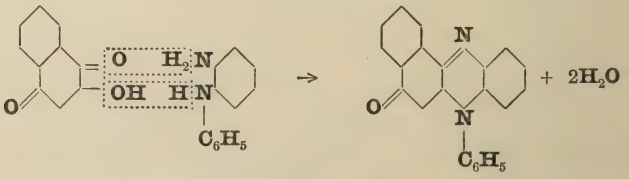


(α-naphthophenazine).

These facts, taken in conjunction with the synthesis of rosinduline by Kehrmann and Messinger (*Ber.*, 1891, xxiv. 587) from oxynaphthoquinoneimide and phenyl-*o*-phenylenediamine



and of rosindone from oxynaphthoquinone and phenyl-*o*-phenylenediamine



clearly show that the rosindulines are derivatives of 4-naphthoquinone-1-imide, and that the indulines are similar derivatives, containing further amido- or substituted amido-groups.

Fast blues (spirit soluble).—Under this name a number of dyestuffs are found in commerce distinguished by the affix R or B, according to the nature of their shade.

They are prepared by heating together amidoazobenzene and aniline hydrochloride for a more or less prolonged period. The longer the heating is continued, the bluer is the dyestuff produced.

For the most part they are used as pigments, but also find application in solutions of ethyl tartaric acid, lævulinic acid, or acetine (prepared by the action of acetic acid upon glycerine), for the purpose of printing upon cotton.

Under these conditions they are known in commerce as Printing blue [A], Acetine blue [B], etc.

Fast blues (soluble).—These dyestuffs are the sodium salts of the sulphonic acids prepared by the sulphonation of the various brands of Fast blue (spirit soluble).

They are used as acid dyes for the dyeing of silk and wool, and are also tannined cotton colours.

Nigrosines from nitrobenzene.—Magenta is formed by the oxidation of aniline, toluidine, nitrobenzene, and nitrotoluene in the presence of iron and hydrochloric acid. Under precisely the same conditions Nigrosines are produced from aniline and pure nitrobenzene.

This method of preparation was discovered by Städeler in 1865, who employed 2 mols. of aniline hydrochloride and 1 mol. of nitrobenzene, and heated the mixture to 230°.

V. Dechend and Wichelhaus (*Ber.*, 1875, viii. 1609) investigated this reaction, and found that by heating nitrobenzene and aniline hydrochloride together with a little iron chloride, at 210° in a sealed tube, a base, $C_{18}H_{15}N_3$ (?), was formed similar in properties to the Azodiphenyl blue prepared from amidoazobenzene and aniline hydrochloride.

The same base is formed by heating together azoxybenzene and aniline hydrochloride in a sealed tube at 230°.

Nigrosines from Nitrophenol.—The formation of these compounds is brought about by heating crude nitrophenol, prepared by the nitration of phenol, with aniline and aniline hydrochloride at 180–200°, until a test portion dissolved in alcohol gives the required shade of colour.

The Nigrosines (spirit soluble) so produced are converted into Nigrosines (soluble) by heating with fuming sulphuric acid at 80°.

Aniline Black.

Runge, in 1834, and, later, Fritzsche (*J. pr. Chem.*, 1840, xx. 454) noticed that, by the oxidation of aniline salts with chromic acid, dark green and blue-black compounds were produced, and in 1843 Fritzsche (*J. pr. Chem.*, 1843, xxviii. 202), by treating aniline hydrochloride with potassium chlorate, obtained a dark indigo blue substance containing 16 per cent. of chlorine.

Perkin also, in 1856, obtained a dark-coloured precipitate by the oxidation of aniline sulphate (containing toluidine) with chromic acid, from which he extracted Mauveïne (see p. 161).

It was subsequently found that this substance could be obtained by the action of other oxidising agents upon aniline, and also by electrolysis (*Goppelsröder*).

The fact that the empirical formula of Aniline black is $(C_6H_5N)x$ (*Goppelsröder*, *Kayser*, and *Nietzki*), and that on energetic reduction it yields di-*p*-diamidodiphenylamine, would seem to show it to be a highly complex induline. Its constitution, however, has not yet been definitely determined. Mild reducing agents convert Aniline black into a leuco-compound, and when it is heated for several hours with fuming sulphuric acid it yields a sulphonic acid soluble in water (*Nietzki*).

The action of sulphurous acid converts Aniline black into a green compound—Emeraldine, which can be considered as an intermediate product in its production, since, on oxidation, it is reconverted into the black.

Aniline black, except as a pigment, is not sold in the finished state, but is always produced upon the fibre.

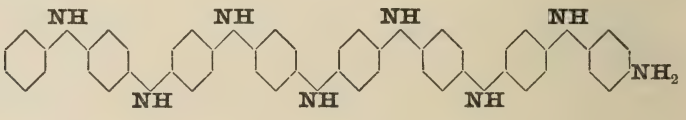
Owing to its fastness it is still one of the most important black dyestuffs, especially for the dyeing of cotton.

The analogous compound, prepared by Piria from naphthylamine, known as *Naphthylamine violet*, is of no practical importance.

Investigations on the chemistry of the Aniline blacks have been conducted by Willstätter and Moore (*Ber.*, 1907, xl. 2665), Willstätter and Dorogi (*Ber.*, 1909, xlii. 2147, 4118), Green and Woodhead, (*J.C.S.*, 1910, xcvii. 2388; 1912, ci. 1117), Green and Wolff (*Ber.*, 1911, xliv. 2570).

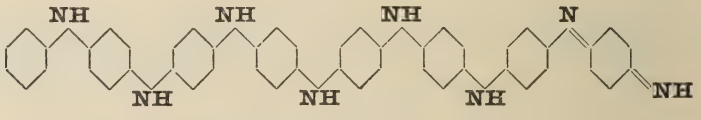
Green and Woodhead have isolated a series of intermediate products in the formation of Aniline black, which may be summarised as follows:—

Leucoemeraldine



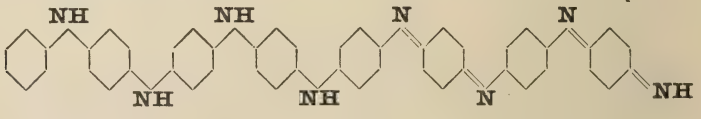
colourless amorphous base.

Protoemeraldine (monoquinonoid stage)



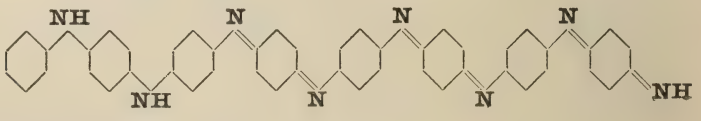
violet base forming yellowish-green salts.

Emeraldine (diquinonoid stage)



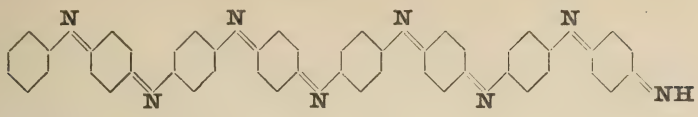
violet-blue base forming green salts.

Nigraniline (triquinonoid stage)



dark-blue base forming blue salts.

Pernigraniline (tetraquinonoid stage)



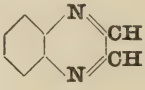
purple base forming purple salts.

It appears therefore that, contrary to the view of Willstätter and his pupils, none of these compounds can be regarded as Aniline black, but they are merely intermediate products in its formation.

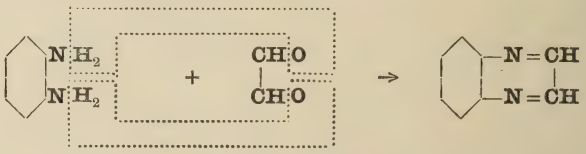
CHAPTER XIX.

QUINOXALINE DYESTUFFS.

These dyestuffs are derivatives of quinoxaline

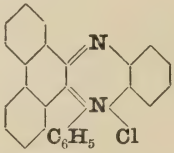


which was prepared by Hinsberg by treating *o*-phenylenediamine with glyoxal



(*o*-phenylenediamine). (glyoxal). (quinoxaline).

The only derivative of this substance which is at present of any technical importance as a dyestuff is *Flavinduline* [B]



which was prepared by C. Schraube (E.P. 18,374[93], A.P. 543,784[95]) by the action of *o*-amidodiphenylamine on phenanthraquinone in glacial acetic acid solution.

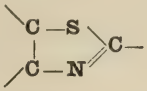
The commercial product is an orange-red powder, soluble in water, which dyes tannined cotton yellow.

It is remarkable that this dyestuff contains no auxochrome group.

CHAPTER XX.

THIAZOL DYESTUFFS.

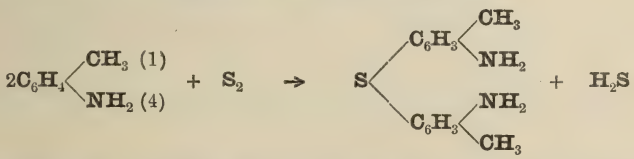
These dyestuffs contain the thiazol ring



and are derivatives of dehydrothiotoluidine.

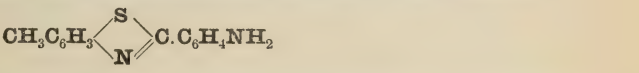
The constitution of this substance has been determined in the following way :—

Merz and Weith (*Ber.*, iv. 393) obtained thiotoluidine by the action of sulphur on *p*-toluidine in the presence of lead oxide at 140°

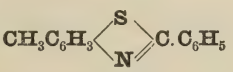


Later, Jacobson (*Ber.*, xxii. 333) and Gattermann (*Ber.*, xxii. 424 ; xxv. 1084) obtained a body containing 4 atoms of hydrogen less, which they prepared by heating *p*-toluidine with sulphur, first for eighteen hours at 180–190°, and then for a further six hours at 200–220°.

This substance they termed dehydrothiotoluidine, and gave it the formula

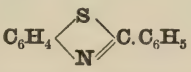


since, on treating it with nitrous acid and boiling with absolute alcohol, it was converted into benzenyl-3 : 4-amidothiocresol

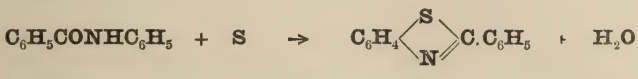


which Hess (*Ber.*, xiv. 493) had prepared by the action of benzoyl chloride on 4-amidothiocresol, $CH_3.C_6H_3(NH_2)SH$.

The lower homologue, benzenylamidothiophenol



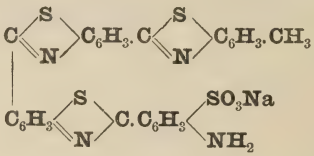
has been prepared by Hofmann (*Ber.*, xii. 2360 ; xiii. 1223), both by the action of sulphur on benzanilide.



and by heating *o*-amidothiophenol with benzoyl chloride.

Dehydrothiotoluidine is not a dyestuff, but if a higher temperature and more sulphur be employed in its preparation, a base is formed which, on sulphonation, yields *Primuline yellow*, a dyestuff discovered by Green in 1887 (*J.S.C.I.*, 1888, vii. 179). It is prepared by heating 2 mols. of *p*-toluidine with 4–5 atoms of sulphur at 200–280°, and subsequently sulphonating the base thus formed with fuming sulphuric acid.

It is evidently a mixture of the sodium salts of the monosulphonic acids of higher dehydrothio-*p*-toluidine derivatives with some of the sodium salt of dehydrothio-*p*-toluidine sulphonic acid; for example, $C_{28}H_{17}N_4O_3S_4Na$



Primuline is a substantive cotton dye, and gives on this fibre a very pure shade of yellow, which, however, owing to its fugitive character, is not of much technical importance.

It can, however, be diazotised upon the fibre and developed with various second components, yielding a number of different colours. This method of producing what are termed the Ingrain colours was first applied to Primuline, and has since been adapted to many of the azo-dyestuffs.

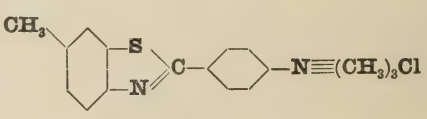
The diazo-salt prepared by diazotising Primuline is extremely sensitive to light, and it is possible to obtain photographic impressions upon cotton cloth by its means.

The method adopted is as follows:—Cotton cloth is dyed with 5 per cent. Primuline and then treated with nitrous acid ($NaNO_2$ sol. acidified with H_2SO_4), and dried in the dark room.

It is then exposed behind a positive for the requisite length of time, when, on developing with an alkaline solution of β-naphthol, the dark portions of the positive will become red, while the light parts will remain uncoloured, owing to the decomposition of the diazo-salt by the action of the light.

Other dyestuffs of this group are:—

Thioflavine T [C]



prepared (E.P. 6319[88], 14,884[88]; A.P. 412,978) by the methylation of dehydrothio-*p*-toluidine with methyl alcohol and hydrochloric or sulphuric acid. It dyes tannined cotton a greenish shade of yellow.

Chloramine yellow [By] is a yellow tannined cotton dyestuff made by the oxidation of dehydrothiotoluidine sulphonic acid.

Thioflavine S [C] is prepared by the methylation of Primuline. It dyes tannined cotton canary yellow.

Mimosa [G] is formed when the diazo-compound of Primuline is treated with ammonia. It dyes unmordanted cotton golden yellow.

Chromin G [K] is related to Thioflavine S, and is made by melting equal molecules of dehydrothiotoluidine with sulphur, methylating, and finally sulphonating with fuming sulphuric acid. It dyes unmordanted cotton from an alkaline bath lemon yellow.

CHAPTER XXI.

QUINOLINE DYESTUFFS.

The base quinoline

is itself not adapted for the preparation of dyestuffs, but, by the entrance of hydrogen atoms into the nitrogen ring it forms tetrahydro-derivatives, which will combine with diazo-salts to form azo-compounds. It can also be converted into dyestuffs of the triphenylmethane series.

Williams in 1856 (E.P. 1090) prepared the first dyestuff of this series—*Cyanine* or *Quinoline blue* [G]—by the action of caustic alkalies on the product of the reaction of amyl iodide on a mixture of equal molecules of quinoline and lepidine.

Its empirical formula is $C_{29}H_{35}N_2I$. This dyestuff is not used in dyeing, but finds application in the colouring of orthochromatic plates for photographic use.

Quinoline red [A] is prepared by the action of benzotrichloride on a mixture of quinaldine

and isoquinoline

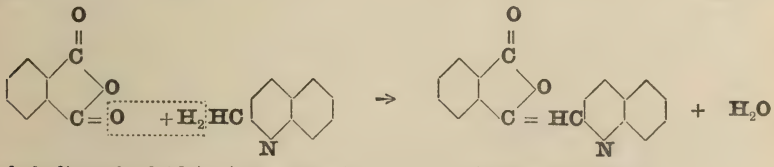
in the presence of zinc chloride. It is probably a triphenylmethane derivative, and, like Cyanine, is used for the production of orthochromatic photographic plates.

For this purpose, mixed with Cyanine, it is found in commerce under the name of *Azaline*.

The most important dyestuff of this group is *Quinoline yellow* S [A], [B], [By], which is the sodium salt of the sulphonic acid made by the sulphonation of Quinoline yellow (spirit soluble)—quinophthalone—with fuming sulphuric acid.

It is an acid dyestuff largely used in the dyeing of silk and wool.

Quinoline yellow (spirit soluble)—quinophthalone—is prepared by the condensation of phthalic anhydride with quinaldine in the presence of zinc chloride



(phthalic anhydride). (quinaldine). (quinophthalone).

CHAPTER XXII.

INDIGOID COLOURING MATTERS.

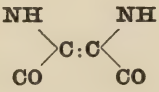
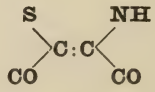
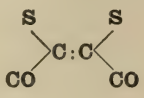
The great increase within recent years in the number of vat colouring matters which are either derivatives of Indigo or analogues of this substance, and which have the chromogen **CO.C : C.CO** in common, has rendered it advisable to divide these compounds into groups.

In the following table (Bohn, *Ber.*, 1910, xliii. 892), the colouring matters have first been divided into two orders, viz. symmetrical and asymmetrical, and each order has then been subdivided into three families, thus :—

Chromogen CO.C : C.CO.

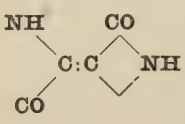
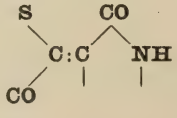
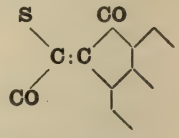
Order I.

Symmetrical (Indigo Type).

Family I.	Family II.	Family III.
Chromogen.	Chromogen.	Chromogen.
		
Indigo and its derivatives.	Ciba violet and its derivatives.	Thioindigo B and its derivatives.

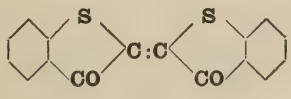
Order II.

Asymmetrical (Indirubine Type).

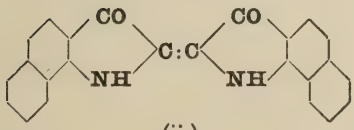
Family IV.	Family V.	Family VI.
Chromogen.	Chromogen.	Chromogen.
		
Indirubine and its derivatives.	Thioindigo scarlet and its derivatives.	Ciba scarlet G and its derivatives.

At the present time some of these families are only represented by one or two members of technical importance, but there is no doubt that in the near future many new colouring matters will be added to this important series, and in the present chapter the order indicated in the table will be followed.

A system of nomenclature for these compounds has been suggested by Jacobson (*Ber.*, 1906, xxxix. 1062) and Friedländer (*Ber.*, 1908, xli. 773). Symmetrically constituted indigos are named from the half-component, with the prefix *bis-*. Thus Thioindigo (i.) is 2.2-bis-Thionaphthene-indigo, and the naphthalene-indigo of Wichelhaus (ii.) is 2.2-bis-naphthindol-indigo.

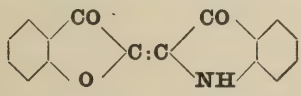


(i.)
(2.2-bis-Thionaphtheneindigo)

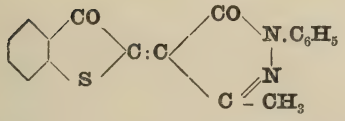


(ii.)
(2.2-bis-naphthindol-indigo).

In the same manner asymmetrical indigos are named thus:—

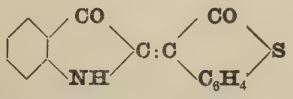


(2-Cumaran-2-indol-indigo).

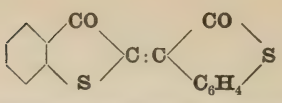


(2-Thionaphthene-2-phenyl-methylpyrazol-indigo).

Indigos of the indirubine type are named thus:—



(3-Thionaphthene-2-indol-indigo).



(2-3-bis-thionaphtheneindigo)
(Thio-indirubine).

1. Indigo and its Derivatives.

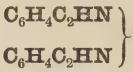
Indigo occurs in a number of plants, especially species of *Indigofera*, in the form of a glucoside—indican—which, on hydrolysis with acids or ferments, is decomposed into Indigo blue (indigotine) and a sugar, indiglucine.

This dyestuff has been known from the earliest times, and even at the present day is the most important of all the colouring matters.

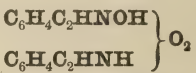
For this reason it has been the subject of investigation by a number of chemists, the first researches being published between 1840 and 1848 by Erdmann, Dumas, Laurent, Liebig, and Fritzsche.

Between 1848 and 1883 a number of constitutional formulæ were proposed for indigo, of which the following are the more important:—

Baeyer, 1868

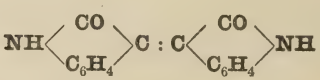


(Indigo).

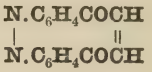


(Indigo white).

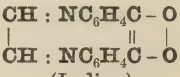
Strecker, 1868



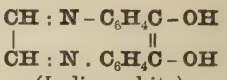
Emmerling and Engler, 1870



E. v. Sommaruga, 1878

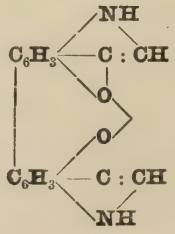


(Indigo).

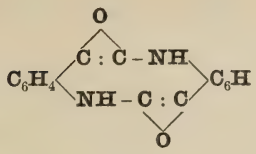


(Indigo white).

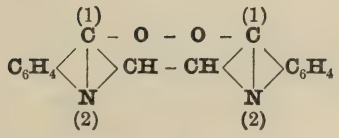
E. Baumann and F. Tiemann, 1879



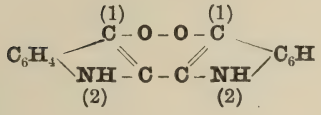
N. Ljubawin, 1879



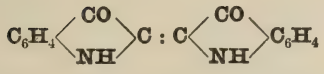
Baeyer, 1882



and

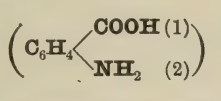


Baeyer, 1883

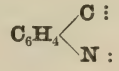


This last formula, which is now the one universally accepted, was arrived at by Baeyer in the following way :—

Earlier researches had proved that Indigo gave isatin on oxidation, aniline when distilled with potash, anthranilic acid



when fused with potash, and nitrosalicylic acid and picric acid when treated with concentrated nitric acid. These researches showed that in indigo at least one benzene ring must be present, and the formation of anthranilic acid indicated the presence of the group



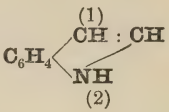
Baeyer in the first instance attempted to reconvert isatin into Indigo by reduction, and in this way in 1868, in conjunction with Knop, prepared dioxindol, oxindol, and indol (*Ann.*, 1868, cxlix. 1, 295).

The relationship between these substances is shown by the following empirical formulæ :—

Indigo, ...	C_8H_5NO *
Isatin, ...	$C_8H_5NO_2$
Dioxindol, ...	$C_8H_7NO_2$
Oxindol, ...	C_8H_7NO
Indol, ...	C_8H_7N

* This was, of course, previous to the determination of the vapour density of Indigo by E. v. Sommaruga in 1879, by which the empirical formula was shown to be double this, *i.e.*, $C_{16}H_{10}N_2O_2$ (*Ann.*, 1879, cxcv. 312).

In 1869 Baeyer and Emmerling (*Ber.*, 1869, ii. 679) synthesised indol by melting crude nitrocinnamic acid with potash and iron filings, and in 1870 (*Ber.*, 1870, iii. 517) gave it the formula



In the same year these chemists also succeeded (*Ber.*, 1870, iii. 514) in converting isatin into Indigo by treating it with phosphorus trichloride, phosphorus, and acetyl chloride, and allowing the intermediate product which is first formed to stand in contact with air.

In the same year Emmerling and Engler (*Ber.*, 1870, iii. 885) succeeded in preparing traces of Indigo by distilling nitroacetophenone with zinc dust and soda lime; and five years later M. Nencki (*Ber.*, 1875, viii. 727) also prepared it by the oxidation of indol with ozone; the yield, however, was extremely small.

Seeing that a close relationship existed between indol and Indigo, Baeyer then decided to attempt the synthesis of Indigo by starting with the compound —*o*-nitrocinnamic acid—from which, with Emmerling, he had succeeded in synthesising indol.

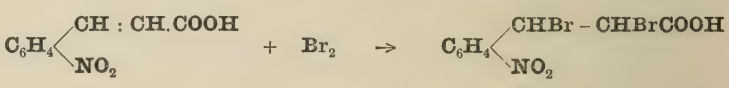
The following equations show the difference in empirical constitution between Indigo, isatin, and *o*-nitrocinnamic acid :—

$C_9H_7NO_4$ less CO_2 and H_2O → C_8H_5NO *
(*o*-nitrocinnamic acid). (Indigo).

$C_9H_7NO_4$ less CO_2 and H_2 → $C_8H_5NO_2$
(isatin).

The first step in the synthesis of isatin would be, then, to remove two atoms of hydrogen from *o*-nitrocinnamic acid.

This Baeyer effected in the following way :—*o*-nitrocinnamic acid combines with bromine to form *α*-*β*-dibrom-*β*-*o*-nitrophenyl propionic acid



Two molecules of hydrobromic acid can be removed from this substance by treatment with alcoholic potash, converting it into *o*-nitrophenyl propiolic acid

This important body, which differs from isatin in containing only one carbon and two oxygen atoms, and from Indigo in having one carbon and three oxygen atoms more, was converted by Baeyer into isatin by boiling with caustic alkali, and into Indigo by heating with caustic alkali in the presence of a reducing agent (grape sugar)

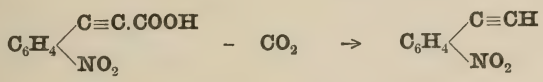
$C_9H_5NO_4$ less CO_2 → $C_8H_5NO_2$
(isatin).

$C_9H_5NO_4$ less CO_2 and O → C_8H_5NO *
(*o*-nitrophenyl propiolic acid). (Indigo).

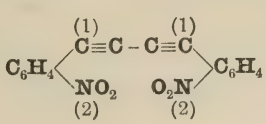
* See footnote, previous page.

This synthesis was effected by Baeyer in 1880, and he also succeeded in preparing Indigo from *o*-nitrophenyl propiolic acid in the following way (*Ber.*, 1882, xv. 50):—

o-nitrophenyl propiolic acid is converted into *o*-nitrophenylacetylene on boiling with water



If the copper compound of this substance is oxidised with an alkaline solution of potassium ferricyanide, di-*o*-nitrophenyldiacetylene is produced



which on treatment with concentrated sulphuric acid yields the isomeric diisatogen, and from this Indigo is formed on reduction with ammonium sulphide.

This synthesis is of importance as showing the existence in Indigo of the carbon chain

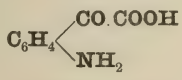
$$C_6H_5.C.C.C.C-C_6H_5$$

The synthetic preparation of Indigo from *o*-nitrocinnamic acid was protected by patents D.P. 11,857 and D.P. 15,516, and a method of printing *o*-nitrophenyl propiolic acid (propiolic acid [B]), together with sodium xanthogenate and borax (D.P. 15,516), was also at one time largely employed.

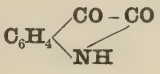
But the yield of Indigo by this method is not satisfactory. In the first place, by the nitration of cinnamic acid only a small proportion of the *ortho*-nitro-derivative is formed, and although this is increased to 70 per cent. by nitrating the ester, a further loss on converting the *o*-nitrophenyl propiolic acid into Indigo causes the process to be too costly for practical purposes. It has now been almost completely replaced by other methods, which will be described later.

The final facts which led to the elucidation of the constitution of Indigo were supplied by an investigation on isatin and indoxyl.

Isatin readily gives metallic compounds which absorb water and pass into salts of isatinic acid. The constitution of this acid and of isatin was given by Kekulé as early as 1869 (*Ber.*, 1869, ii. 748) as



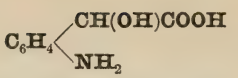
(isatinic acid),

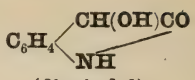


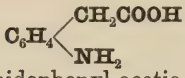
(isatin),

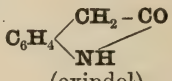
showing isatinic acid as *o*-amidophenyl glyoxylic acid and isatin as its internal anhydride.

This view was later confirmed by Baeyer and Suida (*Ber.*, 1878, xi. 582, 1228; 1879, xii. 1326), and by Claisen and Shadwell (*Ber.*, 1879, xii. 350), who, at the same time, established the constitutions of dioxindol and oxindol, dioxindol as the internal anhydride of *o*-amidomandelic acid, and oxindol as the internal anhydride of *o*-amidophenyl acetic acid


(*o*-amidomandelic acid).

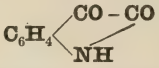

(dioxindol).


(*o*-amidophenyl acetic acid).

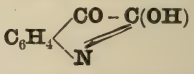

(oxindol).

It soon became apparent that isatin could react in two forms—a labile and a stable—the former being incapable of existence in the free state

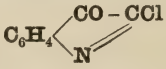
Labile form.[1]


(pseudoisatin or lactam isatin).[2]

Stable form.


(isatin or lactim isatin).[2]

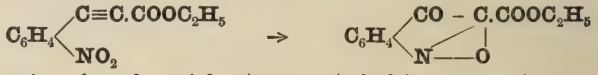
The conversion of isatin into Indigo by Baeyer and Emmerling has already been mentioned (see p. 178), and later (1878) Baeyer (*Ber.*, xi. 1296) found that this transformation could be considerably improved by treating isatin chloride



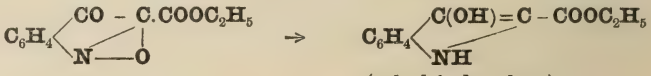
prepared by the action of phosphorus pentachloride upon isatin, with reducing agents.

Indoxyl was synthetically prepared by Baeyer in 1881 (*Ber.*, xiv. 1741) in the following way:—

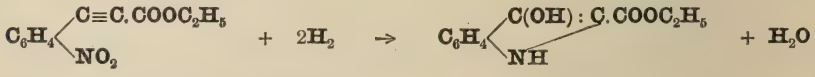
Ethyl-*o*-nitrophenylpropiolate is converted by shaking with concentrated sulphuric acid into the isomeric, ethyl isatogenate (molecular rearrangement)


(ethyl *o*-nitrophenylpropiolate). (ethyl isatogenate).

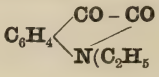
This substance on reduction yields ethyl indoxylate


(ethyl indoxylate),

which is also formed by the action of ammonium sulphide on ethyl-*o*-nitrophenylpropiolate



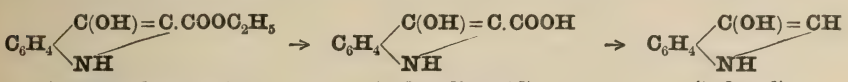
[1] Substitution products of the labile form, such as ethylpseudoisatin



are capable of existence.

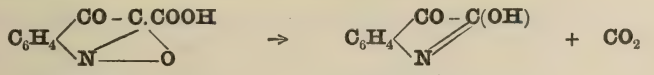
[2] These names were proposed by Baeyer (*Ber.*, xxxiii. (Sonderheft), p. lxv).

Ethyl indoxylate on hydrolysis with caustic soda is converted into indoxylic acid, which, on boiling with water, is converted into CO_2 and indoxyl



(ethyl indoxylate). (indoxylic acid). (indoxyl).

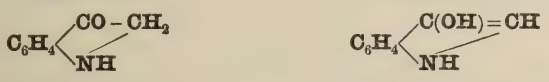
It is also interesting to note that isatogenic acid, prepared from the ethyl salt on hydrolysis, is slowly converted into isatin when a solution of it in sulphuric acid is diluted with water and allowed to stand



(isatogenic acid). (isatin (lactim)).

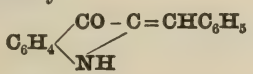
Indoxyl, like isatin, reacts in two forms:—

Labile form. Stable form.



(pseudoindoxyl or ketoindoxyl), (indoxyl or enolindoxyl),

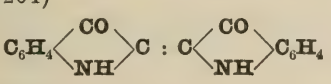
the former being only capable of existence in the form of its derivatives, as, for example, benzylidenepseudoindoxyl



Indoxyl is quantitatively converted into Indigo on oxidation, a fact which was first noticed by Baumann and Tiemann in 1880 (*Ber.*, xiii. 415).

Finally Indirubine, a substance which had been isolated from crude natural Indigo by Schunck (*Ber.*, 1879, xii. 1098), was synthesised by Baeyer (*Ber.*, 1881, xiv. 1745) by combining indoxyl with isatin in alcoholic solution in the presence of sodium carbonate.

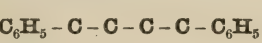
The considerations, therefore, which led Baeyer to publish his formula for Indigo (*Ber.*, 1883, xvi. 2204)



may be summarised as follows:—

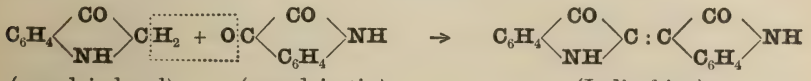
(1) Indigo contains two imido-groups.

(2) The carbon atoms are arranged in it in the same manner as in diphenyldiacetylene, viz.



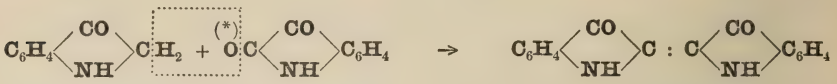
(3) It is formed only from those compounds which contain a ketone group directly attached to a benzene ring.

(4) Formation and properties show it to be closely allied to indirubine, which is prepared from pseudoindoxyl and pseudoisatin according to the equation



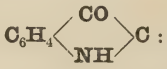
(pseudoindoxyl). (pseudoisatin). (Indirubine)
(β-indogenide of pseudoisatin).

Indigo must therefore be the α-indogenide of pseudoisatin, although its direct formation from pseudoindoxyl and pseudoisatin is not possible, owing to the unreactive character of the α-oxygen atom of pseudoisatin, marked (*) in the equation



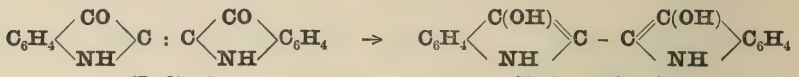
(pseudoindoxyl). (pseudoisatin). (Indigo)
(α-indogenide of pseudoisatin).

Baeyer therefore considered Indigo to be a compound formed by the doubling of the divalent group



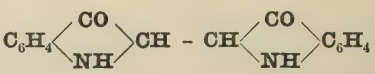
which he termed Indogene, the name indogenide being applied to those bodies containing this group.

Indigo white is formed from Indigo on reduction; it possesses phenolic properties, and its relationship to Indigo is shown by the following formulæ:—



(Indigo). (Indigo white).

Evidently the first action of nascent hydrogen is to form

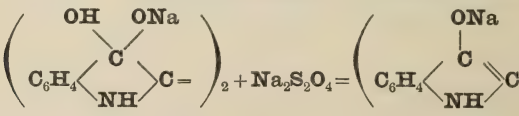


which then passes into its stable (phenolic) form.

The investigations of Binz and his collaborators (*Zeit. für angew. Chem.*, 1906, xix. 1415) show that the reduction of Indigo in the alkaline hydrosulphite vat is preceded by the addition of alkali to the indigo, and can be expressed in the following way:—

(1) $C_{16}H_{10}O_2N_2 + 2NaOH = C_{16}H_{10}O_2N_2.2NaOH$

(2)



(See also Flavanthrene (p. 133).)

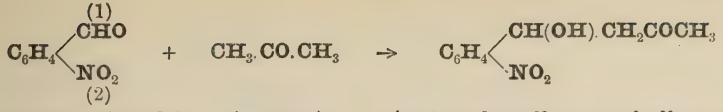
2. Other Syntheses of Indigo.

(1) *From o-nitrobenzaldehyde.*

Baeyer and Drewsen (1882).

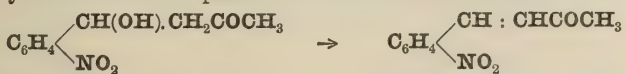
(*Ber.*, 1882, xv. 2856; 1883, xvi. 2205; D.P. 19,768; E.P. 1266[82]; A.P. 257,814 and 257,815.)

The condensation of *o*-nitrobenzaldehyde and acetone yields *o*-nitrophenyllactomethylketone



(*o*-nitrobenzaldehyde), (acetone), (*o*-nitrophenyllactomethylketone),

which readily loses water and passes into *o*-nitroacetocinnamone



(*o*-nitroacetocinnamone),

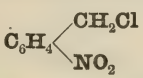
from which Indigo can be prepared on treatment with caustic alkalies.

This method is used technically in the preparation of Indigo salt [K], which is the sodium bisulphite compound of *o*-nitrophenyllactomethylketone, and is employed for printing upon the fibre, the blue being subsequently developed by immersing the material in strong caustic soda solution.

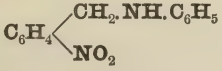
The production of Indigo from *o*-nitrobenzaldehyde has become of considerable importance owing to the discovery by Meister Lucius & Brüning, of Höchst, that *o*-nitrotoluene can be converted into *o*-nitrobenzaldehyde.

This can be brought about by three methods :—

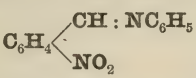
(*a*) The action of chlorine on *o*-nitrotoluene produces *o*-nitrobenzylchloride



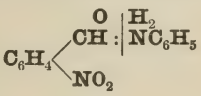
which condenses with aniline to form *o*-nitrobenzylaniline



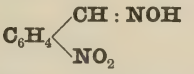
On oxidation this is converted into the corresponding benzylidene derivative



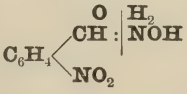
which, on hydrolysis, splits up into *o*-nitrobenzaldehyde and aniline



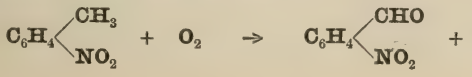
(*b*) *o*-nitrotoluene gives with amyl nitrite, in the presence of sodium ethylate, *o*-nitrobenzaldoxime



which, on hydrolysis with acids, splits up into *o*-nitrobenzaldehyde and hydroxylamine



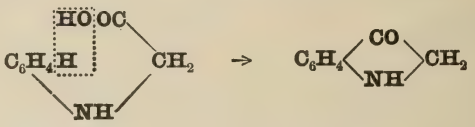
(*c*) *o*-nitrotoluene is converted directly into *o*-nitrobenzaldehyde by oxidation with manganese dioxide and sulphuric acid



(2) *K. Heumann's Synthesis of Indigo.*

(D.P. 54,626; *Ber.*, 1890, xxiii. 3043; Brunck, *Ber.*, 1900, Sonderheft; E.P. 8726[90]; A.P. 622,189.)

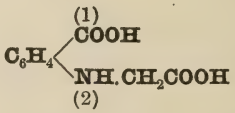
Originally this synthesis consisted in fusing phenylglycine with potash, whereby it became transformed into pseudoindoxyl



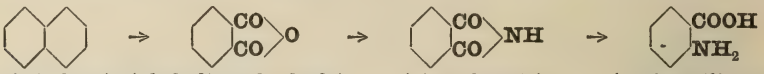
(phenylglycine), (pseudoindoxyl or ketoindoxyl),

from which Indigo can be produced on oxidation.

This method, however, remained of purely theoretical interest[1] until the Badische Anilin und Soda Fabrik of Ludwigshafen-am-Rhein published their completed method for the preparation of Indigo from the corresponding phenylglycine-*o*-carboxylic acid (see Brunck, *Ber.*, 1900, Sonderheft).

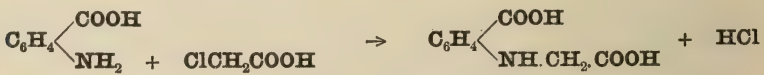


The starting-point in this preparation is naphthalene, which, on treatment with strong sulphuric acid and mercury, is converted into phthalic anhydride. From phthalic anhydride, phthalimide is produced by the action of ammonia, and from this anthranilic acid is formed by the action of chlorine and caustic soda



(naphthalene). (phthalic anhydride). (phthalimide). (anthranilic acid).

Phenylglycine-*o*-carboxylic acid is then prepared from anthranilic acid and chloracetic acid (older method)



(phenylglycine-*o*-carboxylic acid),

and is converted into Indigo by heating with caustic soda.

An intermediate product in this conversion is the carboxylic acid of indoxyl

(phenylglycine-*o*-carboxylic acid), (indoxylcarboxylic acid),

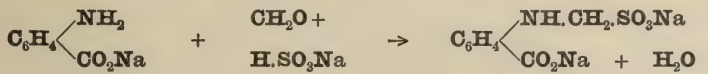
[1] The discovery, however, that the destructive influence of water in the alkali fusion of phenylglycine (see above) could be avoided by melting this substance with sodamide, has led to this process being adopted by Farbwerke vorm. Meister, Lucius, und Brüning.

which can be converted into indigo by treating its alkaline solution with air, and has been used for a considerable time under the name of *Indophor* [B] for the production of Indigo on the fibre.

A newer and better method for converting anthranilic acid into phenylglycine-*o*-carboxylic acid is carried out with the aid of formaldehyde bisulphite and potassium cyanide.

The reaction takes place in three stages:

(1) The addition of formaldehyde bisulphite to sodium anthranilate thus :—



(sodium methylanthranil-ω-sulphonate).

(2) The action of potassium cyanide to form sodium ω-cyanomethylanthranilate thus :—

(sodium ω-cyanomethylanthranilate).

(3) The hydrolysis of the nitrile to sodium phenylglycine-*o*-carboxylate thus :—

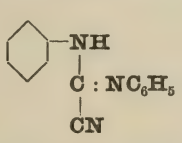
(sodium phenylglycine-*o*-carboxylate).

Another method, closely analogous to the phenylglycine method, consists in condensing aniline and ethylenechlorohydrin to hydroxyethylaniline, $C_6H_5.NH.CH_2.CH_2.OH$, and heating it with caustic potash in an autoclave. The product, on oxidation, gives Indigo (B.A.S.F., E.P. 6225^{04}, $13{,}956^{04}$, A.P. 778,772).

The Indigo prepared by the Badische Company is known as *Indigo pure*, and usually occurs as a paste containing 20 per cent. of Indigo suspended in water; a still more finely divided variety is known as Indigo S.

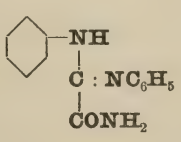
(3) *Sandmeyer's Indigo Synthesis.*

This method consists in converting diphenylthiourea (thiocarbanilide) (from aniline and carbon disulphide) into hydrocyancarbodiphenylimide

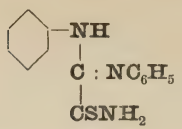


by the aid of potassium cyanide and lead carbonate.

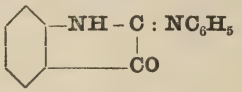
The amide of this



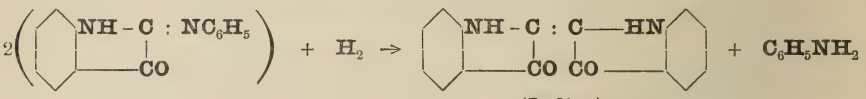
gives the corresponding thioamide on treatment with ammonium sulphide



which, on treatment with concentrated sulphuric acid, yields α-isatinanilide



from which Indigo and aniline are produced by the action of ammonium sulphide



(Indigo).

Indigo or Indigotine is an indifferent substance, insoluble in water and in most of the usual organic solvents, and is therefore of itself of no value as a dyeing agent.

When reduced, however, it is converted into Indigo white, which is of phenolic character and readily soluble in alkalies (see p. 182).

Since it also exhibits a marked affinity for the textile fibres, and is readily reconverted by oxidation into the insoluble Indigo, it is employed in dyeing in the so-called Indigo vat, which is nothing more than an alkaline solution of Indigo white obtained by treating Indigo with some cheap reducing agent.

The material is impregnated with this solution and then exposed to the action of the air, when the Indigo white is reoxidised to Indigo.

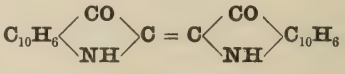
As already mentioned, oxidising agents convert Indigo into isatin, and upon this is based the white discharging of materials dyed with Indigo as well as its various methods of analysis (see p. 340).

Of the derivatives of Indigo the disulphonic acid is of interest.

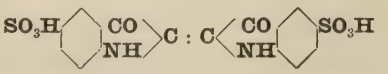
This is found commercially in the form of its sodium salt, *Indigocarmine*,[1] and is prepared by the action of concentrated sulphuric acid upon Indigo. It is an acid dyestuff, formerly much used in the dyeing of wool and silk, but has now been replaced by other colouring matters.

The Heumann synthesis has also been applied to the naphthalene series, and H. Wichelhaus has succeeded in preparing both α- and β-naphthalene indigo from α- and β-naphthylglycine respectively.

They are green dyestuffs having the constitution

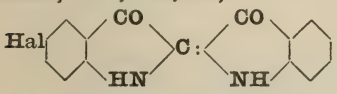


and therefore similar in structure to Indigo blue. They are, however, of no technical importance.

[1]  (Vorländer and Schubart, *Ber.*, 1901, xxxiv. 1860.)

Halogen derivatives of Indigo.

When halogen atoms enter the molecule of indigo in the para-position to the nitrogen atom, the colour of the product does not differ appreciably from that of Indigo itself. Consequently, the 5-halogen indigos (Rahtjen, D.P. 128,575, A.P. 729,217), and the 5 : 5′-dihalogen indigos (Müller, D.P. 30,329, 53,064 ; Jansen, D.P., 112,400)

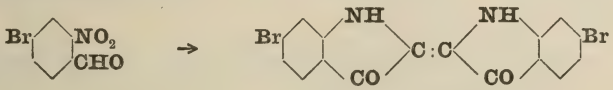


(5-Halogen derivative),

(5 : 5′-dihalogen derivative),

are not technically important. If, however, the halogen atoms enter in the para-position to the carbonyl group, the effect is at once apparent, for the colour of the resulting product is no longer blue, but red-violet.

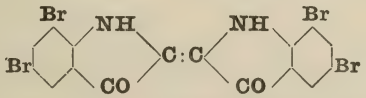
Probably one of the most remarkable discoveries of recent years was that made by Friedländer (*Ber.*, 1909, xlii. 765), who found that the purple of the Ancients, which is derived from *Murex brandaris*, is identical with the 6 : 6′-dibromoindigo which Sachs and Kempf (*Ber.*, 1903, xxxvi. 3303), and Sachs and Sichel (*ibid.*, 1904, xxxvii. 1868), had prepared from *p*-bromo-*o*-nitrobenzaldehyde (Baeyer and Drewsen synthesis, see p. 182).



(6 : 6′-dibromoindigo).

In spite of its great interest from the historical point of view, this colouring matter is not at present manufactured technically, owing to the fact that similar shades can be produced by other means at less cost. It was not until the halogen derivatives of Indigo containing three, four, or more halogen atoms in the molecule had been prepared that the great value of these substances was realised. The first compound of this type to be prepared was 5 : 7 : 5′ : 7′-tetrachloroindigo (Oberreit, F.P. 315,180), which was obtained from the corresponding dichlorophenylglycinecarboxylic acid ; it can also be prepared by the direct chlorination of Indigo (E.P. 28,042[09]) and is known as *Brilliant indigo* B.

Although the tetrachloro derivative can be prepared (although with some difficulty) by the direct chlorination of indigo, the corresponding 5 : 7 : 5′ : 7′-tetrabromoindigo



(5 : 7 : 5′ : 7′-tetrabromoindigo) (Ciba blue 2B [I])

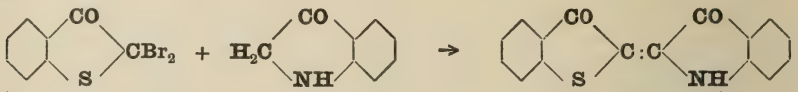
is quite easily obtained by the direct bromination of Indigo ; it is known as *Ciba blue* 2B (E.P. 5122[07], A.P. 856,776) and is of considerable technical importance. The brightness of this vat colour recalls that of the aniline colouring matters, and as, moreover, it retains the fastness to light and washing which is characteristic of the indigoid colouring matters generally, it must be classed among the most valuable of the blue dyestuffs at present in commerce. Numerous compounds of this type have been prepared mainly by the direct halogenation of indigo or indigo white under various conditions, and many of them, of the *Brilliant indigo* class, find considerable application.

It is possible to introduce five or six atoms of halogen into the molecule of indigo if halogenation is carried out in the presence of concentrated sulphuric acid or of chlorosulphuric acid (E.P. 2609[09]). The increase in the number of halogen atoms increases the green shade of the product, but decreases the solubility of the dihydro derivative. A description of many bromo and methoxy derivatives of Indigo is given by Friedländer, Bruckner, and Deutsch (*Ann.*, 1912, ccclxxxviii. 23). *Ciba brown* R [I] is 5 : 7 : 5′ : 7′-tetrabromo-6 : 6′-diamido-indigo (*Ber.*, 1914, xlvii. 2365).

2. Ciba Violet and its Derivatives.

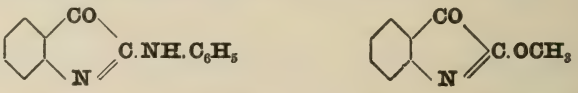
Ciba Violet A (*2-Thionaphthene-2-indolindigo*).—This compound is the simplest member of an important group of colouring matters in which half the molecule is constituted as in indigo, the other half as in thioindigo.

It was originally prepared by Friedländer (*Ber.*, 1908, xli. 776) by the interaction of dibromo-oxythionaphthene and indoxyl in glacial acetic acid solution, thus :—

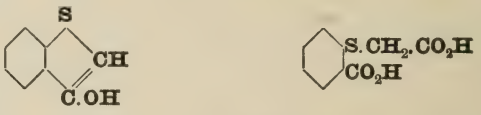


(dibromo-oxythionaphthene). (Indoxyl—Keto form). (Ciba Violet A).

The compound can also be prepared from α-isatinanilide or α-isatin ether



by condensing them with either oxythionaphthene or salicylthioacetic acid (E.P. 11,760[06], 6490[07], A.P. 826,309, 848,356).



It is evident that a large number of colouring matters can be prepared by employing derivatives of the two components mentioned in the above methods of preparation.

Ciba violet is a vat dye, the shade of which lies between the blue of indigo and the red of thioindigo. The halogen derivatives of Ciba violet A occur in commerce under the names—*Ciba violets* (distinguished by various letters), *Thioindigo heliotrope*, and *Thioindigo violet.*

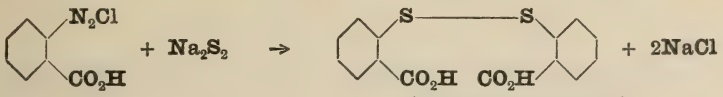
3. Thioindigo and its Derivatives.

Thioindigo B (2 : 2-*bis*-*Thionaphtheneindigo*).—This colouring matter was discovered by Friedländer (*Ber.*, 1906, xxxix. 1060), who obtained it by applying the Badische modification of the Heumann synthesis of indigo (see p. 184) to thiosalicylic acid in place of anthranilic acid.

Thiosalicylic acid can be readily prepared by the following series of reactions :—

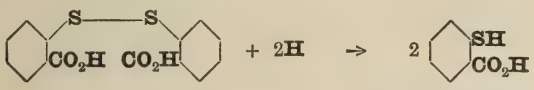
Anthranilic acid is diazotised, and the diazonium salt is converted into dithio-

salicylic acid by the action of sodium disulphide, a substance which may be prepared by dissolving one atom of sulphur in one molecule of sodium sulphide



(Dithiosalicylic acid).

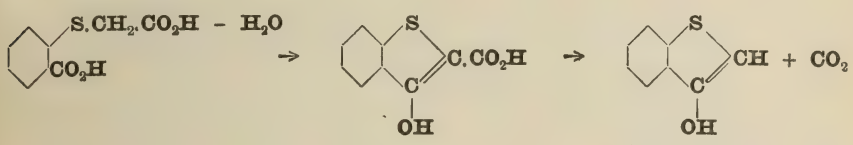
Dithiosalicylic acid is then reduced by iron or zinc to thiosalicylic acid, the sodium compound of which yields phenylthioglycol-*o*-carboxylic acid when condensed with chloroacetic acid.



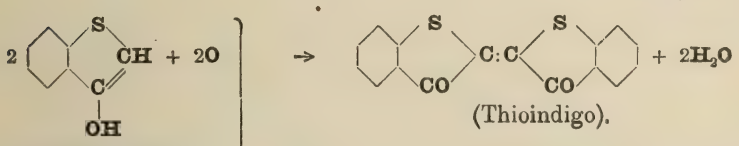
(Thiosalicylic acid).

(Sodium salt of phenylthioglycol-*o*-carboxylic acid).

Phenylthioglycol-*o*-carboxylic acid loses carbon dioxide and water when heated, yielding oxythionaphthene, a substance which passes into thioindigo when oxidised with potassium ferricyanide.

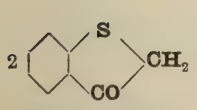


(oxythionaphthene).



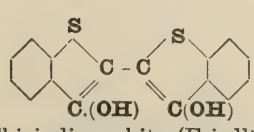
(Enol form);

or



(Keto form).

(Thioindigo).



(Thioindigo white (Friedländer, *Monatsh.*, 1908, xxix. 359)).

The stable form of oxythionaphthene (thioindoxyl), like that of indoxyl, has the enolic structure. It must be remembered, however, that tautomeric substances of this character frequently react as their labile keto forms.

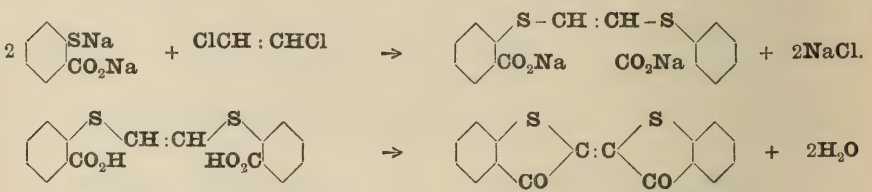
Phenylthioglycollic acid, $C_6H_5.S.CH_2.CO_2H$, which can be prepared in good

yield by the action of benzenediazonium chloride on thioglycollic acid and heating the product

$$C_6H_5N:N:S.CH_2.CO_2H \rightarrow C_6H_5.S.CH_2.CO_2H + N_2$$

is also readily converted into oxythionaphthene (D.P. 177,345).

An important modification of this process for the preparation of thioindigo has been discovered by E. Münch (*Zeit. für angew. Chem.*, 1907, xxi. 2059, D.P. 205,324). This method involves a remarkable condensation of acetylene dichloride with the sodium salt of thiosalicylic acid, by which acetylene-bis-thiosalicylic acid is produced. Thioindigo is directly formed from this substance by the elimination of water



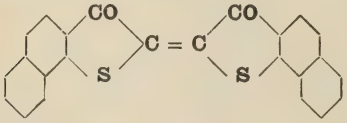
(Acetylene-bis-thiosalicylic acid). (Thioindigo).

Thioindigo can also be prepared from *o*-mercaptoacetophenone $C_6H_4(SH)COCH_3$ (D.P. 202,632).

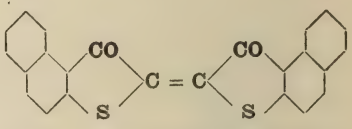
The colouring matter crystallises from a large quantity of xylene as brown-red needles with bronze reflex; it is sparingly soluble in all the usual organic solvents. When heated it sublimes as long needles and can be distilled in small quantities without decomposition.

Alkaline hydrosulphite reduces the compound to the dihydro derivative (thioindigo white) soluble in alkali. Cotton steeped in this vat and exposed to the air is coloured a curious and rather unpleasant shade of red, which, however, possess greater fastness to light than Indigo itself.

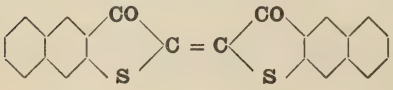
The corresponding derivatives in the naphthalene series have been prepared by Friedländer and Woroshzow (*Ann.*, 1912, cccIxxxviii. 1); they may be summarised as follows:—



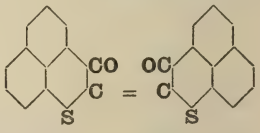
(bis-1 : 2-naphthathiophenindigo).



(bis-2 : 1-naphthathiophenindigo).



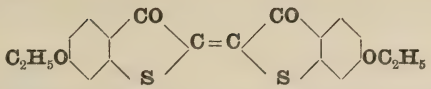
(bis-2 : 3-naphthathiophenindigo).



(bis-1 : 8-naphthaphenthiophenindigo).

Derivatives of Thioindigo.—The entrance of halogen atoms into the molecule of thioindigo increases the blue shade of the compound, and of these *Ciba Bordeaux* B is an example. A greater alteration in the shade is produced when alkyloxy-, alkylthio-, or amino-groups enter the molecule. Thus the entrance of two alkyloxy-groups in the para-position to the carbonyl groups yields

Helindone Orange R



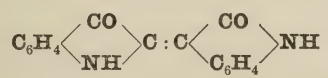
a compound which produces brilliant shades of orange on cotton fibre, and which when dibrominated passes into *Helindone fast scarlet* R.

The presence of alkylthio-groups in place of the alkyloxy-groups in Helindone orange produces *Helindone scarlet* S, and numerous other shades, including brown-orange, dark violet-blue, and even black, can be produced by the introduction of various groups into the molecule of thioindigo. These groups can be introduced either through the halogen derivatives of thioindigo or by starting with a derivative of the parent substance (oxythionaphthene, etc.), from which the thioindigo molecule is formed.

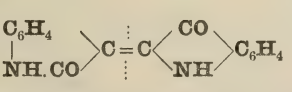
Colouring matters of this kind are as follows:—*Helindone red*, 3B and B; *Thioindigo red*, 3B and BG; *Thioindigo scarlet* S; *Thioindigo orange* R, and *Thioindigo brown* G

4. Indirubine and its Derivatives.

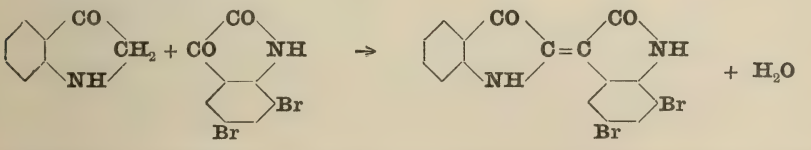
Indirubine, the parent substance of this group, was isolated from natural Indigo by Schunck (*Ber.*, 1879, xii. 1098), and was identified as the β-indogenide of pseudoisatin



by Baeyer (see p. 181). During the early days of the competition between natural and synthetic Indigo, this substance received greater attention than it deserved, mainly because the dyer firmly believed that it was impossible to obtain the same shades with the synthetic product as with the natural colouring matter, because the red indirubine was absent in the pure synthetic compound. As a matter of fact, indirubine is worthless as a vat-colouring matter, since it undergoes fission on reduction, and is then reconverted into Indigo on the fibre (Fasal, *Mitteil. d. Technol. Gewerbemuseums*, Vienna, 1895, xi. 307; compare also Bloxam and Perkin, *J.C.S.*, 1910, xcvii. 1474). A more recent investigation of this reaction (*Proc. Chem. Soc.*, 1909, xxv. 127) shows that both indoxyl and oxindol are formed



The halogen derivatives of indirubine do not suffer under the same disadvantages as indirubine itself, and do not undergo disruption on reduction. A dibromoindirubine can be prepared by the direct bromination of indirubine (D.P. 192,682), but a redder and better shade is formed by the condensation of dibromoisatin with indoxyl



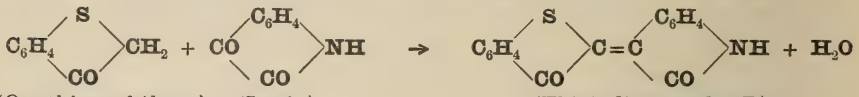
(D.P. 203,437; Friedländer, Bruckner, and Deutsch (*Ann.*, 1912, cccIxxxviii. 40)).

The direct bromination of indirubine with excess of the halogen leads to a tetrabromo derivative which occurs in commerce under the name of *Ciba heliotrope* B [I] (E.P. 6106^{07}, A.P. 876,158).

According to Fasal (*loc. cit.*) indirubinedisulphonic acid is a useful colouring matter, and gives faster shades than the corresponding indigo derivative.

5. Thioindigo Scarlet and its Derivatives.

The instability towards reducing agent which renders indirubine worthless as a vat colour is not shown by those substances which have a sulphur atom in place of one imido group. Thus, if oxythionaphthene replaces indoxyl in the Baeyer synthesis of indirubine, *Thioindigo scarlet* R is produced (E.P. 17,162[06])



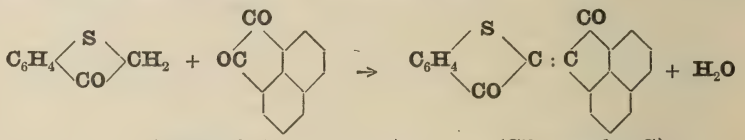
(Oxythionaphthene) (keto form) (Isatin) (Thioindigo scarlet R).

In this compound the unpleasant blue shade of thioindigo is entirely lost; cotton steeped in the reduced vat and exposed to the air is coloured a brilliant scarlet.

Halogen derivatives may be prepared either by the direct halogenation of Thioindigo scarlet or by using dibromoisatin in its preparation. Such compounds are known technically as Thioindigo scarlet G, and Ciba red G.

6. Ciba Scarlet and its Derivatives.

Ciba scarlet G (E.P. 344[08], etc., A.P. 891,690) appears to be at present the only technically important member of this group, and is interesting as being the first colouring matter in the preparation of which the acenaphthene of coal-tar has found application. It is formed by the condensation of acenaphthenequinone with oxythionaphthene in hot acetic acid solution containing a little hydrochloric acid, thus (Bezdzik and Friedländer, *Monatsh.*, 1909, xxx. 284):—

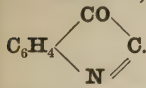
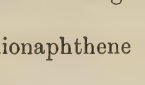
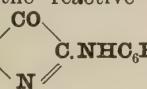
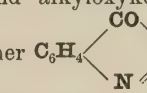


(Acenaphthenequinone). (Ciba scarlet G).

Cotton dyed in the vat of this compound is coloured a brilliant shade of scarlet of considerable fastness. There is no doubt that the colouring matters of this class will find great technical application as soon as a cheap method for isolating acenaphthene has been discovered.

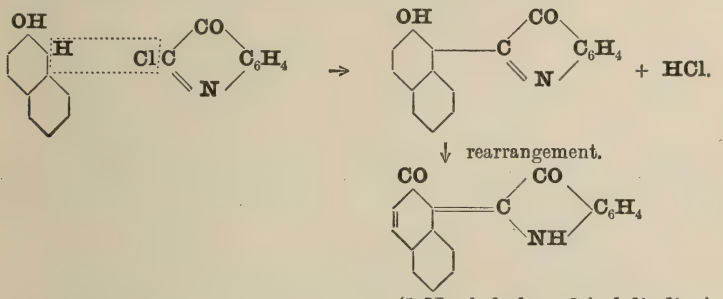
Other Indigoid Colouring Matters.—The short descriptions given above include those indigoid colouring matters which up to the present time have found employment in the industry. It is evident that the number of theoretically possible members of this series, prepared from the various components used in building up the indigoid molecule, is enormous. Many of these colouring matters have been described by Friedländer and his collaborators in a series of papers entitled "On the Indigoid Colouring Matters" (*Monatsh.*, 1908, xxix. 359, 375, 387; 1909, xxx. 271, 871). In the preparation of these substances, any compound which contains the reactive grouping $CH_2:CO$ or $C(OH):CH$ within a ring complex can be used as the first component, such as, for example, indoxyl, thioindoxyl (oxythionaphthene), diketoindene $C_6H_4\langle^{CO}_{CO}\rangle CH_2$, α- and β-naphthol, as well as certain reactive phenols, such as resorcin and *m*-hydroxydiphenylamine.

As second component, practically any cyclic α-diketone can be employed,

such as isatin, β-naphthaquinone, acenaphthenequinone, phenanthraquinone, and the anthrols; also certain reactive α-halogen ketones, such as α-isatin chloride;  dibromo-oxythionaphthene  and dibromopyrazolone, as well as the reactive anilidoketones and alkyloxyketones such as α-isatinanilide  and α-isatin ether 

A few examples will serve to indicate the course of these reactions, and the nature of the indigos formed, thus:—

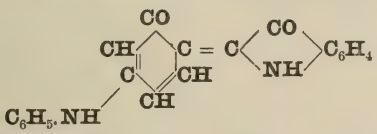
1-Naphthalene-2-indolindigo is formed by the condensation of isatin chloride and β-naphthol in accordance with the equation



(1-Naphthalene-2-indolindigo).

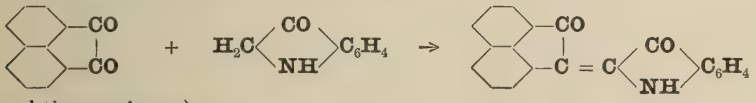
It forms violet-black, glistening needles.

4-Diphenylamine-2-indolindigo is formed in a similar way from α-isatin chloride and *m*-hydroxydiphenylamine. It has the structure



and forms violet needles from alcohol.

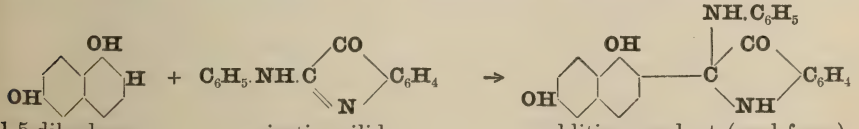
Acenaphtheneindolindigo is produced by the condensation of indoxyl and acenaphthenequinone in acetic acid solution



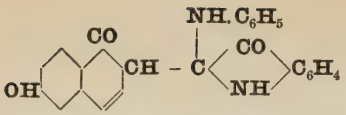
(Acenaphthenequinone).

It forms glistening needles with copper reflex.

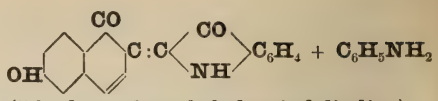
5-Hydroxy-2-naphthalene-2-indolindigo is formed by heating 1 : 5-dihydroxynaphthalene with α-isatinanilide in the presence of 4 to 5 times the quantity of acetic anhydride. The reaction may be represented as taking place in two stages



1-5-dihydroxynaphthalene | α-isatinanilide | addition product (enol form)

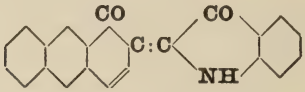


addition product (keto form)

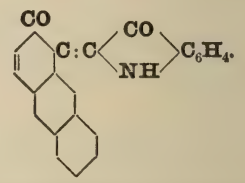


(5-hydroxy-2-naphthaleneindolindigo).

1-Anthracene-2-indolindigo and *2-Anthracene-2-indolindigo* are prepared in an analogous manner from β- and α-anthrol respectively by condensing them with α-isatinanilide in the presence of acetic anhydride. They are represented by the formulæ



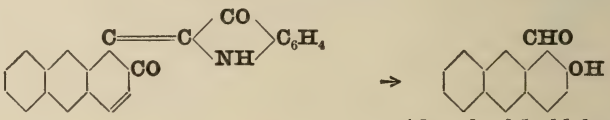
(2-anthracene-2-indolindigo).



(1-anthracene-2-indolindigo).

Both compounds form dark-blue needles with strong metallic reflex. The few examples given above will serve to indicate the vast number of indigoid colouring matters which are capable of isolation, and it is probable that some of them will be used commercially in the near future.

Many of these asymmetrical compounds are, however, unstable towards alkali, and break down under this treatment into the corresponding hydroxy-aldehyde. Thus the 1-anthracene-2-indolindigo mentioned above is transformed into β-anthrol-1-aldehyde when warmed with 30 per cent. caustic alkali



(β-anthrol-1-aldehyde).

When this change is effected by dilute alkali, it, of course, renders the compound valueless as a colouring matter, since it will undergo partial disruption in the formation of the vat.

CHAPTER XXIII.

THE SULPHUR OR SULPHIDE DYESTUFFS.

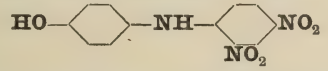
The term "sulphur" or "sulphide" dyestuffs is given to those colouring matters which are produced by heating certain organic materials with sulphur and sodium sulphide (fusing with these substances or boiling with sulphur and aqueous sodium sulphide), and does not therefore include such dyestuffs as Methylene blue, Thioindigo, etc., which also contain sulphur.

The sulphide dyestuffs are soluble in a solution of sodium sulphide, and cotton is dyed direct from this solution.

The first member of the series was prepared in 1873 by Croissant and Bretonnière, who fused various organic materials, such as sawdust, bran, etc., with sodium sulphide and named the product, Cachou de Laval. This substance dyes cotton greenish-yellow shades, which change to brown on exposure to the air. The colour is fast to washing, but only moderately fast to light. The fastness to light is improved, and rendered exceptionally good, by an after treatment with copper salts or a mixture of copper and chromium salts. It was formerly largely used for dyeing browns and dark shades generally which had to stand cross dyeing. It has now been replaced by stronger and purer products of analogous type.

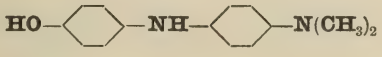
Some twenty years later Vidal found that certain derivatives of the benzene and naphthalene series could be used with advantage in the production of sulphide dyestuffs; thus Vidal black was prepared by fusing *p*-aminophenol with sulphur and sodium sulphide.

A great advance was made in the year 1897 by the discovery of Immedial black, prepared by heating *p*-hydroxy-*o'p'*-dinitrodiphenylamine



(obtained by condensing *p*-aminophenol with 1-chloro-2 : 4-dinitrobenzene) with sulphur and sodium sulphide, this being the first sulphide dyestuff to give a true black shade; earlier so-called blacks were really of a brownish-black shade.

This discovery led to a rapid development of investigations in this field, and the next step in advance to be recorded is the production of Immedial pure blue, a bright, pure blue dyestuff prepared from *p*-dimethylamino-*p'*-hydroxydiphenylamine

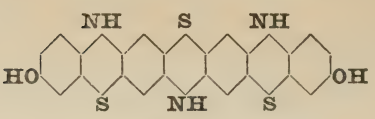


(obtained by heating dimethyl-*p*-phenylenediamine hydrochloride with *p*-aminophenol).

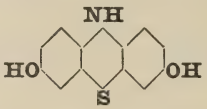
The first red sulphide dyestuff, prepared from aminohydroxyphenazine, soon afterwards made its appearance, and this was followed by the important yellow and orange colouring matters, Immedial yellow and Immedial orange, both obtained from *m*-tolylenediamine.

As regards the constitution of the sulphide dyestuffs, extremely little is known. Generally speaking, the blue and black dyes are derivatives of thiodiphenylamine, the yellow and brown are derived from thiazole, the red from azines (and contain the azine ring unchanged), and those sulphide colouring matters which do not contain nitrogen are considered to be derived from phenols.

Vidal regarded the constitution of the Vidal black from *p*-aminophenol as

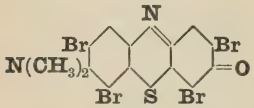


since he found that by carrying out the reaction at a lower temperature, dihydroxythiodiphenylamine



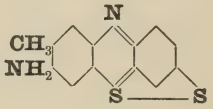
was formed, but the experimental basis for this supposition is very slight.

Immedial pure blue has been examined by Gnehm and his pupils. By oxidation and bromination the dyestuff yields tetrabromodimethylaminothiazine



(the position of the bromine atoms is not certain), thus demonstrating the presence of the thiazine ring in the dyestuff.

Immedial indone, also, which is prepared from a mixture of *p*-aminophenol and *o*-toluidine, from the analysis of its condensation product with chloroacetic acid, is considered (Frank, *J.C.S.*, 1910, xcvii. 2044) to have the formula



The following table gives the names of some of the more important dyestuffs of this series and the raw materials from which they are manufactured :—

Dyestuff.	Made from	Firm and Patents.
Immedial yellow D	*m*-tolylenediamine.	Cassella, E.P. 11,771/02.
Eclipse yellow G, 3G	mono- and di-formyl-nitrotoluidine or *m*-tolylenediamine.	Geigy, E.P. 23,967/02.
Immedial yellow GG	dehydrothiotoluidine.	Cassella, E.P. 4097/06.
Immedial brown B	*p*-hydroxydinitrodiphenylamine.[1]	Cassella, E.P. 25,754/99.
Immedial orange C	*m*-tolylenediamine.	Cassella, E.P. 11,898/02.
Immedial maroon B	aminohydroxyphenazine.	Cassella, E.P. 14,836/00.
Thion blue B	*p*-nitro-*o*-amino-*p'*-hydroxydiphenylamine.	Kalle, E.P. 19,332/01.
Immedial blue C	*p*-hydroxy-*o'p'*-dinitrodiphenylamine.	Cassella, E.P. 25,234/97.
Immedial pure blue	*p*-dimethylamino-*p'*-hydroxydiphenylamine.	Cassella, E.P. 16,247/00.
Immedial indone	indophenol from *p*-aminophenol and *o*-toluidine.	Cassella, E.P. 58/02.
Hydron blue	indophenol from carbazole and nitrosophenol.	Cassella, E.P. 2918/09.
Immedial black NN	dinitrophenol.	Cassella, E.P. 19,831/96.
Immedial black V extra	*p*-hydroxy-*o'p'*-dinitrodiphenylamine.	Cassella, E.P. 25,234/97.
Sulphur black T extra	dinitrophenol.	Berlin Co., E.P. 1151/00.
Thiophenol black T extra	dinitrophenol.	Soc. Chem. Ind. Basle, E.P. 13,035/03.

[1] This is first boiled with alkali hydroxides and the product then treated as usual.

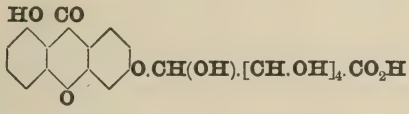
For a detailed account of the sulphide dyestuffs see *Die Schwefelfarbstoffe, ihre Herstellung und Verwendung*, O. Lange, 1912, and *J. Soc. Dyers*, 1917, xxxiii. 3.

CHAPTER XXIV.

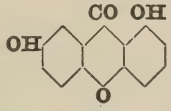
XANTHONE DYESTUFFS.

Indian Yellow or Puiri is prepared at Monghyr in India by evaporating the urine of cows fed on mango leaves.

Its principal constituent is the magnesium salt of euxanthic acid, a glucoside having the formula

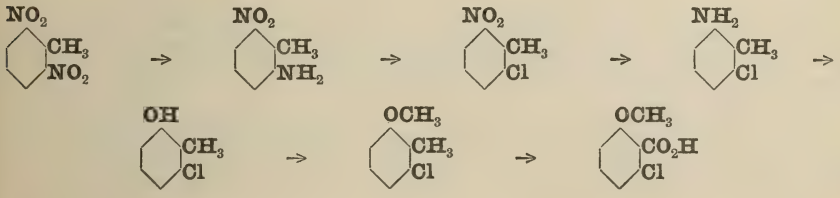


which, on hydrolysis, splits up into glycuronic acid and euxanthone, a dihydroxyxanthone of the formula

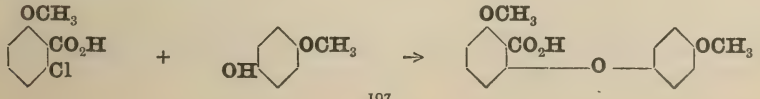


Euxanthone has been synthesised by the following series of reactions (Ullmann and Panchaud, *Ann.*, 1906, cccl. 108) :—

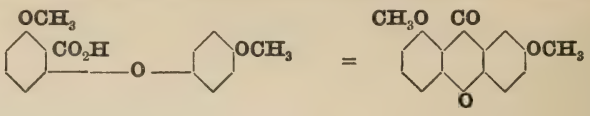
2 : 6-Dinitrotoluene is reduced to nitrotoluidine, the amino-group of which is replaced by chlorine according to Sandmeyer's reaction. The other nitro-group is now reduced, and the resulting amino-group is replaced by hydroxyl by means of the diazo reaction. This hydroxyl group is methylated and the 1-chloro-6-methoxytoluene which is produced is oxidised to the corresponding benzoic acid, thus :—



The 2-chloro-6-methoxybenzoic acid is now condensed with hydroquinone monomethyl ether, using copper powder as catalyst, and dimethoxyphenylsalicylic acid is produced

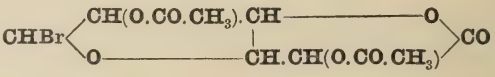


With concentrated sulphuric acid this yields euxanthone dimethyl ether



from which euxanthone is obtained by treatment with aluminium chloride in benzene solution.

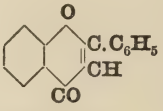
Euxanthic acid has been synthesised from Euxanthone (Neuberg and Neimann, *Zeit. physiol. Chem.*, 1905, xliv. 115) by condensing it with diacetylbromo-glycuronolactone



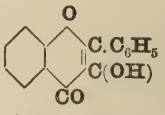
(prepared from glycuronolactone and acetyl bromide) by means of potassium methoxide.

Flavone and Flavonol Dyestuffs.

In 1895 St von Kostanecki published his investigations on the nature and synthesis of certain natural colouring matters, which, under the names Quercetin, Fisetin, Luteolin, Rhamnetin, etc., had been used from the earliest times as yellow mordant dyestuffs. v. Kostanecki succeeded in establishing these dyestuffs as derivatives of Flavone and Flavonol.



(Flavone),

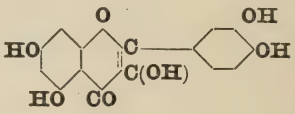


(Flavonol),

and has, in many cases, prepared them synthetically.

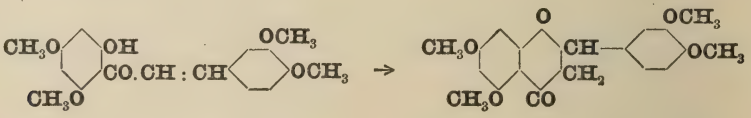
The following are the most important dyestuffs of this group:—

Quercetin,

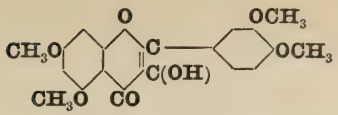


which is the colouring principle of quercitron, has been synthesised as follows (Kostanecki and Tambor, *Ber.*, 1904, xxxvii. 793; Kostanecki, Lampe, and Tambor, *ibid.*, 1402):—

2'-Hydroxy-4' : 6' : 3 : 4-tetramethoxychalkone is heated in alcoholic solution with dilute hydrochloric acid for 24 hours, when 5 : 7 : 3' : 4'-tetramethoxy-flavanone is produced

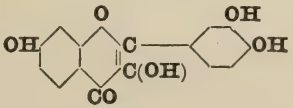


The *iso*nitroso-derivative of the latter, when boiled with acetic acid containing sulphuric acid, furnishes 5 : 7 : 3' : 4'-tetramethoxyflavonol



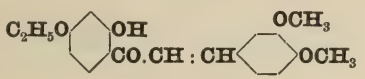
and this, when treated with hydriodic acid, gives 5 : 7 : 3′ : 4′-tetrahydroxyflavonol, which is identical with natural quercetin.

Fisetin,

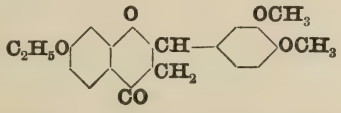


the colouring principle of young fustic, has been synthetically prepared as follows (Kostanecki, Lampe, and Tambor, *Ber.*, 1904, xxxvii. 784) :—

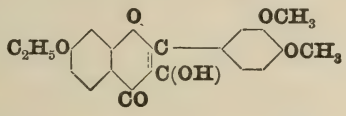
Resacetophenone monoethyl ether and veratraldehyde are condensed to 2′-hydroxy-4′-ethoxy-3 : 4-dimethoxychalkone



which is boiled first with alcoholic sulphuric acid and then with absolute alcohol, whereby 7-ethoxy-3′ : 4′-dimethoxyflavanone



is produced. The *iso*nitroso-compound of this is boiled with an acetic acid solution of sulphuric acid, being thereby converted into 7-ethoxy-3′ : 4′-dimethoxyflavonol

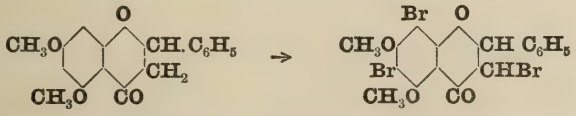


and this on being boiled with hydriodic acid furnishes 7 : 3′ : 4′-trihydroxyflavonol or fisetin. (See also Kostanecki and Nitkowski, *Ber.*, 1905, xxxviii. 3587.)

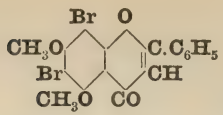
Chrysin was discovered by Piccard in poplar buds, and was found by him to have the empirical formula $C_{15}H_{10}O_4$. He also found that when boiled with potash it was decomposed into phloroglucinol, benzoic acid, acetic acid, and acetophenone.

The synthesis has been carried out as follows (Kostanecki and Lampe, *Ber.*, 1904, xxxvii. 3167) :—

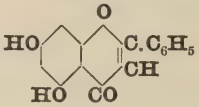
5 : 7-Dimethoxyflavanone is converted into the tribromo-derivative



which, when treated with alcoholic potash, gives 6 : 8-dibromo-5 : 7-dimethoxyflavone

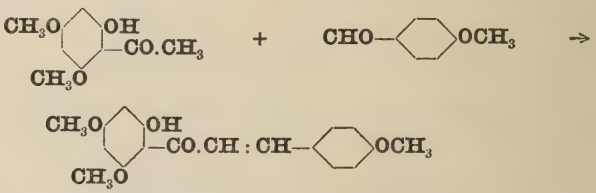


and this, on being heated with hydriodic acid, yields chrysin

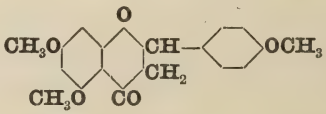


Apigenin is obtained by hydrolysing the glucoside apiin occurring in parsley; its synthesis is carried out as follows (Kostanecki, Oenike, and Tambor, *Ber.*, 1904, xxxvii. 792; see also Czajkowski, Kostanecki, and Tambor, *ibid.*, 1900, xxxiii. 1988):—

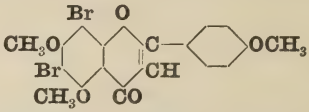
Phloracetophenone dimethyl ether and anisaldehyde are condensed to give 2′-hydroxy-4′ : 6′ : 4-trimethoxychalkone



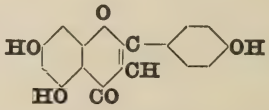
which, with alcoholic sulphuric acid, yields 5 : 7 : 4′-trimethoxyflavanone.



The tribromo-derivative of this yields, with alcoholic potash, 6 : 8-dibromo-5 : 7 : 4′-trimethoxyflavone

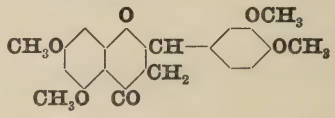


which, with hydriodic acid, is converted into 5 : 7 : 4′-trihydroxyflavone or apigenin

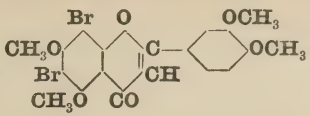


Luteolin, the colouring principle of weld extract, is 5 : 7 : 3′ : 4′-tetrahydroxyflavone. It has been synthesised by the following series of reactions (Fainberg and Kostanecki, *Ber.*, 1904, xxxvii. 2625; see also Diller and Kostanecki, *ibid.*, 1901, xxxiv. 1449):—

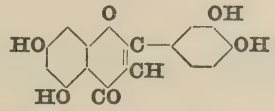
5 : 7 : 3′ : 4′-Tetramethoxyflavanone



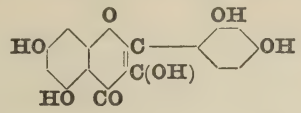
is converted through the tribromo-derivative into dibromotetramethoxyflavone



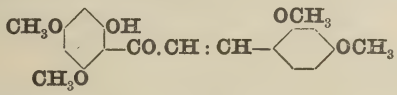
which, with hydriodic acid, yields luteolin



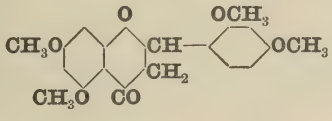
Morin, which occurs in fustic, has the constitution



and has been synthesised from 2′-hydroxy-4′ : 6′ : 2 : 4-tetramethoxychalkone



by condensing it with alcoholic hydrochloric acid to 5 : 7 : 2′ : 4′-tetramethoxyflavanone



The *iso*nitroso-derivative of this yields, with acetic and sulphuric acids, a trimethoxy-compound which, with hydriodic acid, is converted into 5 : 7 : 2′ : 4′-tetrahydroxyflavonol or morin (Kostanecki, Lampe, and Tambor, *Ber.*, 1906 xxxix. 625). (Further information as to naturally occurring dyestuffs will be found in Rupe's *Die Chemie der natürlichen Farbstoffe* (Parts I. and II.) and Abderhalden's *Biochemisches Handlexikon*, vol. vi.)

CHAPTER XXV.

A SHORT REVIEW OF THE SYNTHETIC DYESTUFFS.

(Compare Dr H. Caro, *Ueber die Entwicklung der Theerfarbenindustrie*, Berlin, 1893.)

The first artificial dyestuffs were Picric acid, prepared in 1771 by Woulfe from Indigo and nitric acid; and Rosolic acid (Aurine), discovered by Runge in 1834. Neither of these compounds were, however, manufactured on the commercial scale owing to the then considerable cost of the materials from which they were derived; and it was not until 1855 that a technical method was introduced for the production of Picric acid from coal-tar.

The era of the synthetic dyestuffs dates, however, from the discovery of Mauveïne in 1856 by W. H. Perkin, and its commercial manufacture in 1857 by Perkin & Sons at Greenford Green, near London.

Perkin's discovery, that a colouring matter could be produced by the oxidation of aniline, led to the study of the behaviour of this base towards various oxidising agents, with the result that in 1859 Verguin prepared Fuchsin (Magenta) by the oxidation of crude aniline by means of tin chloride, and manufactured it in conjunction with the firm of Renard Frères, of Lyons.

Magenta had, however, been previously prepared by Natanson in 1856 from aniline and ethylenechloride, and in 1858 by A. W. Hofmann from aniline and carbon tetrachloride.

In 1860 the method of preparing Magenta by oxidising aniline with arsenic acid was introduced by Nicholson, Girard, and de Laire; and in the same year Girard and de Laire prepared the first blue synthetic dyestuff—Rosaniline blue—by treating Magenta with aniline.

The recognition by Hofmann of the nature of this reaction, *i.e.* the phenylation of Rosaniline—led him to try the effect of introducing alkyl groups instead of phenyl groups into the Rosaniline molecule, and by this means he prepared Hofmann's violet in 1863.

In 1862 Nicholson made the important discovery that Rosaniline blue could be converted into a sulphonic acid by treating it with sulphuric acid, and that the sodium salt of this sulphonic acid was soluble in water; soluble Rosaniline blue (Water blue, Nicholson's blue) was in this year manufactured by the firm of Simpson, Maule, & Nicholson, and in the same year Aniline black was first prepared by Lightfoot.

As early as 1861 Lauth had prepared Methyl violet by treating dimethylaniline with oxidising agents; but it was not until 1866 that, in conjunction with Ch. Bardy, he introduced a method for the technical production of dimethylaniline, and consequently of Methyl violet, which in 1867 was technically prepared by Poirrier and Chappat.

This dyestuff quickly replaced Hofmann's violet.

The first green synthetic dyestuff was Aldehyde green, discovered in 1862 by Cherpin; but it was quickly replaced by Iodine green (Keisser, 1866), which, in

its turn, gave way to Methyl green, prepared by the action of methyl chloride on Methyl violet (Wischin, 1873).

During this period Nicholson (1861) isolated Chrysaniline from the Magenta melt, and its nitrate was manufactured under the name of Phosphine.

The nitrobenzene process for the manufacture of Magenta was discovered by Coupier in 1866, and led him in the following year to prepare the first soluble Induline.

A spirit-soluble Induline had, however, been prepared in 1863 by Dale and Caro.

The decade 1860–1870 also witnessed the introduction of Bismarck brown (Martius, 1863), Martius yellow (1864), Palatine orange (1869), and Magdala red (Clavel, 1868).

Meanwhile the Kekulé benzene theory had been established, thus opening up a new era in the manufacture of the synthetic dyestuffs. The former purely empirical researches then gradually gave way to well-directed scientific syntheses; and the constitutions and mode of production of the various compounds already prepared were step by step elucidated.

The first example of such synthesis is afforded by the synthetic production of Alizarine by Graebe and Liebermann in 1868; and its commercial production by the method of Graebe, Liebermann, and Perkin in 1869.

Whilst the chief attention of chemists was occupied with the synthesis of Alizarine, another class of dyestuffs—the azo-compounds—appeared in 1876 in commerce.

The azo-compounds themselves had already been discovered by Griess, and their constitution elucidated by Kekulé; moreover, one member of this group—Bismarck brown—had already been prepared, since 1863, on the commercial scale. It was not until 1875, however, that Caro discovered Chrysoidine, and also indicated the technical value of the Griess method of preparing azo-compounds.

In the same year Roussin prepared the Oranges, and Liebermann and Ullrich succeeded in transforming Alizarine into its sulphonic acid.

When the azo-dyestuffs were first introduced, it was considered that only orange and yellow dyestuffs could be formed by this means. This idea was, however, dispelled by the discovery of Fast red A by Caro in 1878.

This year also saw the introduction of a number of important dyestuffs, amongst others being Alizarine blue, Malachite green, and the Ponceaux.

In the preparation of the last-named, the important naphthol and naphthylamine sulphonic acids were, for the first time, used commercially, and their great value as second components in the preparation of azo-dyestuffs indicated.

The year 1878 also witnessed the commercial manufacture of Galleïne and Cœruleïne, dyestuffs which had previously been prepared by Baeyer in 1871.

In all the azo-compounds mentioned above, the sulphonic acid group plays an important part, and the application of Nicholson's method of sulphonation to other members of the triphenylmethane series enabled Caro in 1887 to prepare Acid magenta, Acid violet, etc.

The first disazo-dyestuff—Biebrich scarlet—was prepared by Nietzki in 1879, and in the same year Caro prepared the important nitro-dyestuff, Naphthol yellow S.

The year 1880 witnessed the completion of the Baeyer synthesis of Indigo, and in 1883 the introduction of Phosgene gave rise to the Phosgene colours (Caro and Kern). The first of these dyestuffs— Crystal violet—appeared in this year, and was followed by a number of colouring matters of the same class.

In 1884 Böttiger discovered the fact that Congo red was substantive to cotton —a discovery which gave rise to the preparation during the following decade of

a vast number of azo-compounds from Benzidine and allied bases, which constitute the important group of the substantive cotton azo-dyestuffs.

In this year, also, Tartrazine was prepared.

In 1888 the property possessed by fuming sulphuric acid of introducing hydroxyl groups into Alizarine and its derivatives was discovered by Bohn, and in the following year was applied to the preparation of a number of valuable dyestuffs by R. Schmidt.

In the same year the Oxazines were introduced, as well as the Rosindulines, by Fischer and Hepp.

In 1899 formaldehyde was applied to the synthesis of dyestuffs by the Höchst Farbwerke, leading, not only to the synthesis of new members of the triphenylmethane series, such as New magenta, but also to the production of the Pyronine and Acridine dyestuffs.

At this period the method of producing insoluble azo-compounds directly on the fibre was indicated by the discovery of Primuline in 1887 by Green.

The year 1897 marks the introduction of synthetic Indigo by the Badische Co., and the process has been so improved since then that it appears likely that the natural product will ultimately be displaced.

Halogen (particularly bromo-) derivatives of Indigo have been prepared, and are now much used in dyeing.

Of recent years great advances have been made in the synthesis of vat dyes (dyeing like Indigo), and the first red vat dye of this class was Thioindigo red, discovered by Friedländer and placed in the market in 1906. This was followed, in 1907, by Thioindigo scarlet. Vat dyes of the anthracene series have also been extensively manufactured, of which perhaps Indanthrene is the most important. Great activity has also been displayed of late in the manufacture of sulphide dyestuffs amongst which Sulphur black T and the Immedial blues and blacks are important. The constitution of these substances still, however, remains unsolved.

It will thus be seen that the general trend of the dyestuff industry to-day is in the direction of the production of fast colouring matters, and it would appear that this object may be best attained in the field of the vat dyestuffs.

PART II.—PRACTICAL.

CHAPTER XXVI.

THE TECHNICAL LABORATORY.[1]

There are certain differences between the technical or works laboratory and that usually found in Universities and in Technical Schools; and, although the preparations and technical operations described in the following pages can all be carried out in the ordinary scientific laboratory, yet in cases where a laboratory can be set apart for purely technical work (as is the case in chemical and other works, and in the larger chemical schools) a few details as to the arrangement and fittings of such a laboratory may be here given. (The general arrangement and construction of chemical laboratories and their fittings is admirably described by Russell, *The Planning and Fitting-up of Chemical and Physical Laboratories*, Batsford, London, 1903.) In the first place, the space apportioned to each worker must be much greater than that usually allowed, even in an advanced scientific laboratory. Not only is the work carried on on a larger scale, but the technical student or chemist will often be able to have half a dozen different experiments going on at one and the same time. Thus he will perhaps start a sulphonation experiment at the beginning of the day which requires only slight attention for the regulation of the temperature. A condensation requiring a flask and reflux condenser takes up a good deal of room, and generally proceeds for several hours by itself without any attention beyond an occasional test. During the morning, too, there will be several substances, left from the day before, to be filtered at the pump; and, finally, it may be necessary to stir mechanically as many as half a dozen or more beakers, which alone would occupy an ordinary student's bench. It is often very convenient, also, to set apart a whole or a portion of a bench for the purposes of analysis; upon which will stand several burettes containing standard solutions, and adjacent to which may be a shelf or shelves containing the more generally used chemicals and reagents. Besides this, the laboratory should contain at least one large draught chamber, a large sink with draining-board and draining-pegs, and enough space to accommodate one or more autoclaves and other large pieces of apparatus. Wide shelves should be fixed round the sides of the laboratory, or in a suitable place, for holding large bottles and tins as well as apparatus. If there is no dye-house or dyeing laboratory in connection with the technical laboratory, an experimental dye-bath should also be provided. The benches may be constructed of pitch pine or stained American white-wood, and should be fitted with drawers for storing corks, test and filter papers, etc., and a wide shelf underneath. The top of the bench may be of teak, but in technical laboratories

[1] The term "technical" used in this work refers, of course, only to that branch of applied organic chemistry specially dealt with.

it is often made of ordinary wood upon which is sheet-lead. In this case a hard-wood fillet is screwed to the edge of the bench-top, projecting up about $\frac{3}{4}$-inch, and the lead is dressed over the top of it. If the bench is double, *i.e.* arranged for work on each side of it, a channel should run down the centre, to carry away waste water from turbines, condensers, etc. If against the wall, the channel will be at the back.

The laboratory must, of course, be supplied with the usual gas and water connections; in many cases it is useful to have electricity also, for electrolytic work and driving small motors for stirring, shaking, etc.; finally, steam can usually be easily fitted, especially in chemical works.

The gas pipes should run along the front of the benches, and small branches carrying taps are fitted at convenient distances along it, over which a rubber tube can be slipped. In the case of a lead-covered bench, as described above, each gas branch is bent neatly over the top of the fillet; but where an ordinary straight teak top is fitted, a semicircle of wood is cut out of the edge of the teak

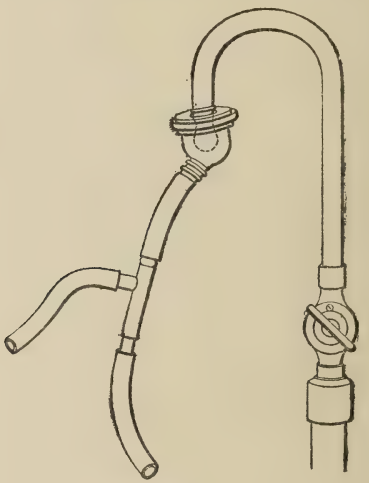


Fig. 1.

(3 inches diameter), in place of which is the gas branch so arranged that no part of this is above the level of the table. This is by far the best arrangement of the gas pipes, as, in case of accident, the gas is easily turned off at the front of the bench, and also there is no danger of accidentally breaking glass flasks, etc., by contact with a protruding gas jet. (This is the arrangement in the chemical laboratories at Heidelberg.)

Besides the ordinary gas-fittings, there should be one or two specially large branches, on a free wall side if possible, to which a large Fletcher burner can be fixed for heating autoclaves, large pans, etc.

For each worker there must be arranged a suction pump and a mechanical stirrer.

The former, to be used for filtering and all operations conducted under diminished pressure, is best arranged by soldering a water pipe to a metal pump. These (which cost about three shillings) cannot be satisfactorily united with the water supply by rubber tubing. A piece of ordinary rubber tubing is fitted to the exit tube of the pump, to carry away the waste water, and a piece of thick-walled tubing—"pump tubing"—attached to the side-tube. This pump tubing may either be connected directly with the filter-flask or with one or more T-pieces carry-

ing glass taps, so as to allow two or more attachments to the suction. In existing laboratories, where no provision has been made for filtering under reduced pressure, it is exceedingly convenient to join a rubber-lined brass "union" to the metal pump by means of a short length of lead pipe, and then to attach this temporarily to the water pipe when required. The "union" should of course fit fairly tightly when slipped over the nozzle of the water pipe. In this way half a dozen metal pumps will enable a large number of workers to filter with suction at their own benches (see fig. 1).

For driving the mechanical stirrers or agitators either water or electric power is used.

In the case of the former, a small Rabe's turbine is either permanently fixed at a suitable point and connected with the water supply by means of a lead pipe soldered to it, or a rubber-lined brass "union" is soldered to the inlet tube

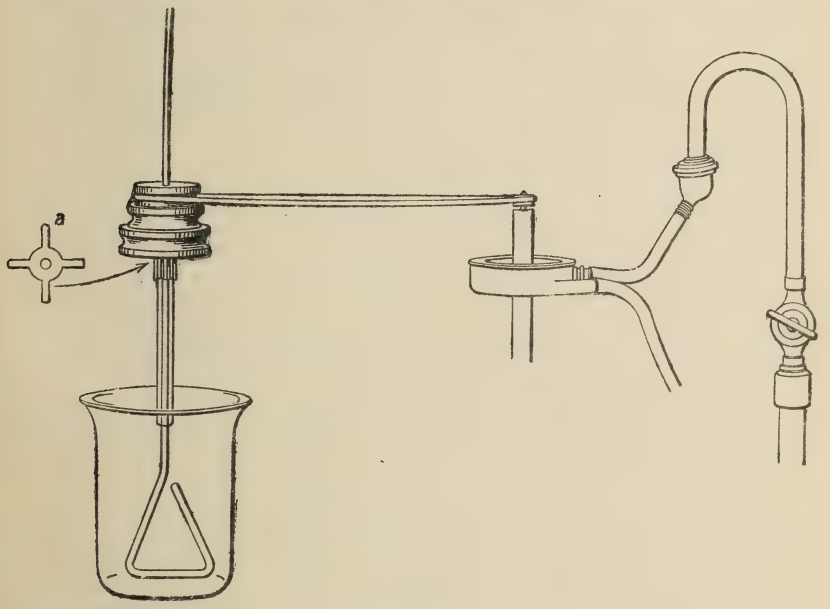


Fig. 2.

of the turbine, so that the latter may be fixed to any water pipe in the laboratory. A wide rubber tube is attached to the exit pipe of the turbine in order to carry off the waste water.

If a small electric motor is used to provide the power, this is fixed in a suitable position on the working bench.

The stirring arrangement consists of a suitably bent glass rod, the straight part of which passes through corks fixed in the hollow axis of a wooden grooved wheel (see fig. 2). The whole is held firmly in the clamp of a retort-stand by means of the brass (or glass) tube through which the glass rod passes, friction between the revolving wheel and the top of the tube being avoided by interposing a tin support which is cut in the shape shown, the four arms being bent up at right angles to the centre part (fig. 2, *a*). The stirrer is driven from the motor or turbine wheel by means of an endless rubber cord. A piece of solid rubber cord about 3 feet long is chosen, and the ends cut at a very acute angle. The tapering parts are laid together and bound firmly with stout thread.

If the union is neatly done, there will be no tendency for the cord to become displaced when in use. Several stirrers are easily driven simultaneously by connecting them in series by such endless rubber cords.

A very necessary adjunct of the technical laboratory is the library. This should be well stocked with the standard works on the subject, as well as the periodicals treating upon this branch of Applied Chemistry.

The following list includes the more important works on the subject:—

I. General Literature (excepting Patent Literature).

Lunge, *Coal-Tar and Ammonia*, 1916.
Warner, *Coal-Tar Distillation*, 1913.
Lunge, *Technical Methods of Chemical Analysis*, English translation edited by Keane, Vol. II. Part ii., 1911.
Nietzki (translated by Collin and Richardson), *Chemistry of the Organic Dyestuffs*, 1892.
Harmsen, *Die Fabrikation der Theerfarbstoffen und ihrer Rohmaterialien*, 1889.
Schultz, *Die Chemie des Steinkohlentheers*, 3rd ed., 1900–1901.
Ristenpart, *Chemische Technologie der organischen Farbstoffe*, 1911.
Georgievics, *Lehrbuch der Farbenchemie*, 1913.
Bucherer, *Lehrbuch der Farbenchemie*, 1914.
Seyewetz and Sisley, *Chimie des Matières Colorantes Artificielles*, 1896.
L. Lefèvre, *Les Matières Colorantes Artificielles*, 1896.
Wahl (translated by Atack), *The Manufacture of Organic Dyestuffs*, 1914.
Meldola, *Coal and what we get from it*, S.P.C.K., 1905.
Schultz and Julius (translated and added to by Green), *Survey of the Organic Colouring Matters*, 1904.
Thorpe, *Dictionary of Applied Chemistry* (new edition, 1912). Special Articles.

II. Special Works on Certain Branches.

Reverdin and Fulda, *Tabellarische Uebersicht der Naphtalinderivate*, 1894.
Täuber and Norman, *Derivate des Naphtalins*, 1896.
Walter, *Aus der Praxis der Anilinfarbenfabrikation*, 1903.
Mühlhäuser, *Die Technik der Rosanilinfarbstoffen*, 1889.
Lange, *Die Schwefelfarbstoffe, ihre Herstellung und Verwendung*, 1912.
Felsen, *Der Indigo und seine Konkurrenten*, 1909.
Felsen, *Türkischrot und seine Konkurrenten*, 1911.
Staeble, *Die neueren Farbstoffe der Pigmentfarben-Industrie*, 1910.
Heermann, *Koloristische und textilchemische Untersuchungen*, 1903.
Schwalbe, *Benzol-tabellen*, 1903.
Rawson, Gardner, and Laycock, *Dictionary of Dyes, etc.*, 1901.
Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, 2nd ed., 1910.
Mulliken, *Identification of the Commercial Dyestuffs*, 1910.
Green, *The Analysis of Dyestuffs*, 1915.
Binz, *Verwendung der wichtigeren Organischen Farbstoffe*, 1905.
Gardner, *The British Coal-Tar Industry*, 1915.

III. Works dealing specially with Patent Literature.

Heumann, Friedländer, and Schultz, *Die Anilinfarben und ihrer Fabrikation.*
Friedländer, *Fortschritte der Theerfarbenfabrikation*, several volumes from 1877 onwards.
Winther, *Patente der Organischen Chemie*, 1908.
English Patents Abridgments. Class 2.

IV. Periodicals.

Journal of the Chemical Society.
Journal of the Society of Chemical Industry.
Journal of the Society of Dyers and Colourists.
The Dyer.
Zeitschrift für Farben und Textil Industrie.
Revue Générale des Matières Colorantes.

A useful selection of the above, for the English-speaking student, would be Meldola, Warner, Atack, Green (*Analysis*), and Gardner.

Harmsen gives good accounts of the plant used on the large scale, whilst Nietzki is more of a theoretical book; the 5th German edition (*Chemie der organischen Farbstoffe*) appeared in 1906.

Schultz gives a fairly full account of the raw materials (vol. i.) and colouring matters (vol. ii.) obtained from coal-tar.

Lefèvre and, in a less degree, Seyewetz and Sisley give full lists of the known colours.

Schultz, Julius, and Green give a list of all known dyes with their formulæ and literature. Green has added to his translation of the original German a useful introduction dealing with the raw materials. A 5th German edition (Schultz, *Farbstofftabellen*) was published in 1914.

The special articles in the new edition of Thorpe's *Dictionary of Applied Chemistry* will be found particularly useful.

Of the second class, Täuber and Norman give a very full account of the derivatives of naphthalene used technically, and Schwalbe describes in the same way the compounds of the benzene series used for the same purpose. Walter describes, in minute detail, the manufacture of Safranine.

Of the Patent Literature, the German works are reprints of German patents, differently arranged.

General Operations.

Besides the ordinary operations which the student or technical chemist will have become acquainted with before using this book,[1] there are many which are more specially applicable to technical work, and these will, therefore, be here described (see also Wolfrum, *Chemisches Praktikum*, Theil II., Engelmann, 1903).

Preparation of materials.—In nearly all chemical preparations much time and trouble may be saved if the solid materials are in a finely divided state. Even if the substance to be used has to be dissolved in a solvent in which it is easily soluble, yet if large lumps of it are employed, complete solution takes a long time. Hard substances are best powdered in a mortar and finally passed through a fine wire or hair sieve. Most of the organic substances, however, which are used in the following preparations may be easily reduced to powder by grinding them in an ordinary metal coffee-mill. When a substance which melts easily in hot water has to be brought into solution—such as, for

[1] **Hewitt**, *Organic Chemical Manipulation*, Whittaker & Co.
Garrett and **Harden**, *Elementary Course of Practical Organic Chemistry*, Longmans, Green & Co.
Cohen, *Practical Organic Chemistry for Advanced Students*, Macmillan.
Gattermann and **Schober**, *Practical Methods of Organic Chemistry*, Macmillan.
Lassar-Cohn and **Smith**, *Laboratory Manual of Organic Chemistry*, Macmillan. See also **Lassar-Cohn**, 4th German edition.

instance, α-naphthylamine or phenol—it is, of course, not so necessary to carry out this preliminary powdering.

In all cases the use of powdered caustic soda, which can now be easily obtained, is preferable to using stick or lump caustic.

Zinc dust should be passed through a fine sieve before use; and "iron powder," nearly as fine as zinc dust (which can be obtained from most chemical agents), is of very great use in carrying out reductions where the ordinary iron filings are almost useless (on the laboratory scale).

Heating.—The simplest case of heating in the technical laboratory is the maintenance of the contents of a flask at the boiling-point. The flask is usually fitted with a cork bored to allow the passage of the inner tube of a condenser, and sometimes also, through a second hole, a thermometer or glass tube. The condenser is supported, whenever possible, in a slanting position, so that any moisture condensing on the outside may not drop on, and perhaps crack, the hot flask. The latter rests either on a sand-bath, which is heated directly with a bunsen burner, or on the ring of a water-bath. When it is necessary to shake the flask frequently, a short, wide piece of glass tube is passed through the cork and connected with the reflux condenser by means of a 4-inch piece of rubber tubing.

In many cases, *e.g.* in sulphonation processes, it is necessary to maintain a flask at a definite temperature for several hours. This is done by heating in a suitable bath of water, solution of calcium chloride, or oil, which is kept at the right temperature by means of a thermo-regulator. This is arranged as follows:—A glass tube about 8–10 mm. in diameter is bent in the form of a circle and closed at one end. The open end is sealed to a fairly wide capillary tubing which is bent up at right angles to the circular tube. This latter rests on the bottom of the bath, and the capillary tube passes up the side and is again bent at right angles over the side of the bath; it is here united with the gas regulator. This consists of a U-tube with side branches on each limb, and one end is closed by a tap carrying a small thistle funnel (see fig. 3). Mercury is poured into the tube to the height shown, and the regulator is connected to the circular tube by one of the side-tubes, while the other is connected with the burner by means of a piece of rubber tubing. The glass tube conveying the gas to the regulator passes into the limb till it just touches the surface of the mercury, and the lower end is cut at an acute angle, so that as the mercury rises and falls the flow of gas is gradually regulated. The circular glass tube is filled with air (for high temperatures) or 10 per cent. calcium chloride solution.

In order that the flame may never be extinguished, a by-pass can be arranged by uniting the inlet and outlet gas tubes by a third rubber tube carrying a screw-clip; but it is perhaps better to arrange a small independent jet burning just over the bunsen burner, made of a blowpipe jet or a piece of fine copper tube. By this arrangement a bath may easily be kept within two degrees for any length of time.

It is often necessary to heat to boiling large quantities of liquids, as in the case of boiling out lime salts, iron residues, etc., and this is best done by passing in a current of steam. If steam is laid on in the laboratory, this is easy; but if not, the steam is generated by heating a large tin-can fitted with a straight safety tube. The substance to be heated may be placed in a large enamelled iron pan or even a stoneware pneumatic trough.

Heating under pressure.—For heating substances under pressure an autoclave is used. The inner vessel is not filled more than three-quarters full with the mixture to be heated, and the materials should be well stirred and mixed together unless a vessel fitted with a stirrer be used. Round the edge is a

groove in which a lead ring is placed. The lid is then put on, the lead ring serving the purpose of making a tight joint. In screwing up the nuts and bolts, they are first screwed by the fingers as far as possible, and then the wrench is used. It is best to turn the nuts half or once round in rotation till they are all quite tight. If one is screwed tightly before the others, leakage may occur, or a nut may slip from its place.

The lid of the autoclave is supplied with a pressure-gauge and a thermometer-pipe. A little oil is placed in the latter before introducing the thermometer. Observations of both temperature and pressure are usually made in heating the autoclave; indications of the pressure-gauge, for instance, often show when a reaction is finished.

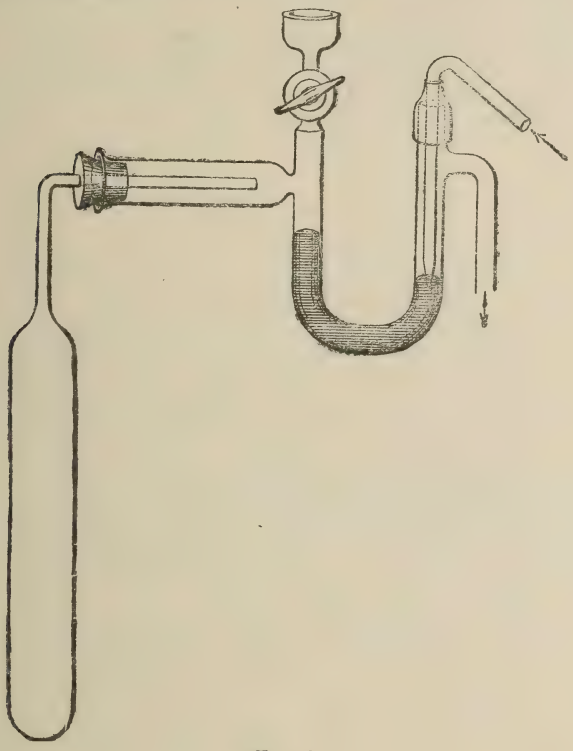


Fig. 3.

The vessel is heated either by the direct flame or in an oil-bath. In the latter case the bath is usually a part of the apparatus. When the direct flame is used, great care must be taken to raise the temperature very slowly to the required point, and the autoclave must not be opened till it is quite cold.

Work with fuming sulphuric acid.—Fuming sulphuric acid is used very largely technically for the preparation of polysulphonic acids, etc.; and as it is a very unpleasant substance to handle if proper precautions are not taken, it is necessary to explain what these are.

Acid containing SO_3 up to nearly 40 per cent. is usually liquid, from 40 per cent. to 60 per cent. solid, from 60 per cent. to 70 per cent. liquid, and from 70 per cent. upwards again solid. The acid, if solid, is first melted. This is done by

first withdrawing the stopper and placing a watch-glass on the mouth of the bottle or vessel containing the substance, and then leaving it in a warm place till melted. If a stove or warm room is not available, the bottle is placed on a layer of sand in a large vessel, surrounded by sand, and warmed with a very small flame. When the contents of the bottle are melted, the neck is wiped dry inside and fitted with a cork carrying two glass tubes, one of which reaches to the bottom of the bottle. The other end of this tube is bent like a siphon and ends in a glass tap. The second tube passes only a short distance through the cork and is bent at right angles.

The fuming acid is now easily ejected from the bottle by connecting the short tube with the compressed air (or an ordinary foot-bellows) and opening the tap. The acid may be blown over with the mouth if care be taken to interpose a cylinder or bottle containing lumps of caustic soda.

If the acid is too strong (for analysis, see p. 300), it is diluted by pouring into ordinary concentrated sulphuric acid. As much heat is given out during the mixing, the fuming acid must be added slowly.

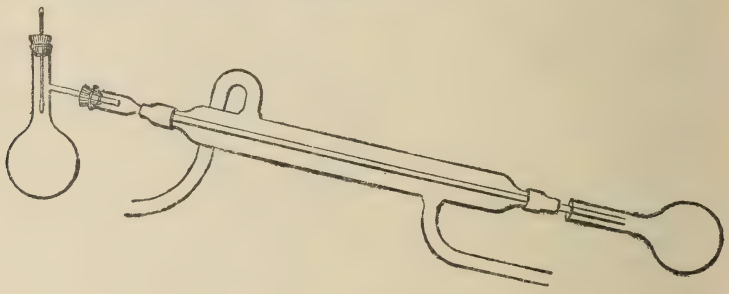


Fig. 4.

An example will show how the quantities are calculated :—

Required 360 grams of acid containing 25 per cent. SO_3; to be made from an acid containing 40 per cent. SO_3 and concentrated acid (96 per cent. H_2SO_4).

Let x = the weight of fuming acid to be taken
and y = the weight of conc. sulphuric acid,

then $\frac{4y \times 80}{100 \times 18}$ is the weight of SO_3 necessary to combine with the 4 per cent. of water in the conc. acid, and we have

i. . . . . $\frac{40x}{100} - \frac{8y}{45} = 90$

ii. . . . . $x + y = 360$

whence $x = 266{\cdot}5$ and $y = 93{\cdot}5$. Therefore 266·5 grams of the 40 per cent. SO_3 acid must be mixed with 93·5 grams conc. sulphuric acid in order to give 360 grams of an acid containing 25 per cent. of SO_3.

Distillation.—The distillation of liquids is carried out in various ways, depending on (1) the boiling-point, and (2) the state of the liquid as regards its admixture with other substances.

In the case of liquids boiling at temperatures up to about 130–140°, the vapours are condensed by passing them through a tube surrounded by a water-jacket (Liebig's condenser); when the boiling-point lies between 140° and about 280°, an ordinary tube two or three feet long is used; and above 280° the

distillation is usually carried on under diminished pressure. When, however, the distillation is carried on very slowly (as in the distillation of crude benzene for testing purposes), an uncooled tube is used.

Distillation of pure liquids or homogeneous mixtures of liquids.—The apparatus used consists of a distilling flask fitted with a thermometer, the bulb of which is just below the side tube; the latter is fitted to a condenser (straight tube or Liebig's) by means of a cork (fig. 4). No rubber corks should be used in any part of the apparatus. The liquid is placed in the flask so that the latter is not more than two-thirds full, and a small piece of porous porcelain dropped in, so as to induce regular boiling. The liquid is heated by means of the water-bath, or with the free flame.

Fractional distillation.[1]—If the separation of two or more liquids into their constituents has to be carried out, a fractionating column is used. This is fitted into an ordinary wide-necked flask, and effects a more complete separation by condensing the higher boiling portions and returning them to the flask.

Of the many kinds of condensing columns sold, that of Young is the best. In fractional distillation the liquid is distilled and the distillate collected in fractions. The number of fractions depends on the boiling-points of the constituents and many other factors, so that it is impossible to give a general rule for the procedure.

Having obtained a number of fractions, the lowest boiling one is redistilled within the same limits as before. It will be found, of course, that the whole does not pass over. When the limit has been reached, the second fraction is added to the residue in the distilling flask and the distillation recommenced. Now, although the whole of the second fraction was collected at a temperature *above* the limit just referred to, yet a part of it will now pass over *below* this point. Two separate portions distilling within the same limits have been thus collected, and these are of course mixed together. The distillation is now continued in exactly the same way; when the limiting temperature of the second fraction has been reached, the third fraction is added to the residue in the flask, and so on. In this way, after mixing the distillates boiling within the same limits, it will be found that some have become very large and others have diminished. In the simple case of a mixture of two liquids whose boiling-points lie far apart, the separation will be fairly complete after carrying out the fractionation described. When, however, three or more liquids are mixed together, the fractions lying between the boiling-points of the pure liquids are refractionated repeatedly till a very complete separation has been effected.

Fractional distillation is carried out on the large scale principally in the separation of benzene, toluene, and xylene from crude benzols and toluols.

The composition of the three brands of commercial benzene is approximately as follows:—

Name.	Benzene, per cent.	Toluene, per cent.	Xylene, per cent.
90 per cent. benzol, . .	75	24	1
50 ,, ,, . .	50	40	10
30 ,, ,, . .	10	60	30

An example of the fractional distillation of "50 per cent. benzol" will illustrate the process (Cohen, *Practical Organic Chemistry*, p. 123).

200 c.c. were distilled fractionally, using a simple column with two bulbs.

[1] See *Fractional Distillation*, S. Young, 1904, Macmillan.

Seven fractions were collected in the first distillation, and a residue left in the flask as follows :—

A 71·5–85°.	B 85–90°.	C 90–95°.	D 95–100°.	E 100–105°.	F 105–110°.	G 110–115°.	Residue.
19 c.c.	53 c.c.	26 c.c.	15 c.c.	13 c.c.	17 c.c.	21 c.c.	33 c.c.

(It will be noticed that this sample more than fulfils the requirement for a 50 per cent. benzol, as 113 c.c. distilled over up to 100° instead of 100 c.c.)

A smaller distilling flask is now taken and the first fraction A is redistilled.

Distilled A till temperature was 79°, 5 c.c. collected.
Now add B collect at 79–81°, 42 c.c. ; at 81–85°, 10 c.c.
„ C „ 81–85°, 9 c.c.
„ D and E „ 85–105°, 50 c.c.
„ F „ 105–108°, 11 c.c.
„ G „ 108–110°, 22 c.c.
Residue, . . . 42 c.c.

The 5 c.c. first collected is technically known as first runnings, and contains hydrocarbons of the fatty series, etc.

There is a large fraction (42 c.c.) at the boiling-point of benzene (80°), and a smaller one (22 c.c.) at the boiling-point of toluene (110°).

The fractions collected at 81-85° (19 c.c.) were redistilled, giving 12 c.c. at 79–81° and 7 c.c. at 81–85°. Further, the fraction collected at 105–108° (11 c.c.) was redistilled, giving 6 c.c. at 105–108° and 5 c.c. at 108-110°. By these last two fractionations the amount of benzene is increased by 12 c.c. and of toluene by 5 c.c. The total crude benzene obtained is thus 54 c.c. and toluene 27 c.c., and by a further fractionation fairly pure benzene and toluene are obtained.

On the large scale nothing is lost, for the intermediate fractions and residues are either refractionated or used direct for purposes where a pure product is not needed.

The above example may be tabulated, for the sake of greater clearness, as follows :—

	A′ below 79°.	B′ 79–81°.	C′ 81–85°.	D′ 85–105°.	E′ 105–108°.	F′ 108–110°	Residue.
A . . .	5 c.c.	...	...	...	...	...	...
Added B .	...	42 c.c.	(10 c.c.*)	...	...	...	...
Added C .	...	...	(9 c.c*)	...	...	...	...
Added D, E	...	...	...	50 c.c.	...	...	...
Added F .	...	...	...	...	(11 c.c.*)	...	...
Added G .	...	...	...	...	...	22 c.c.	42 c.c.
*Refractionated—							
C′. .	...	12 c.c.	7 c.c.	...	...	...	...
E′. .	...	...	...	...	6 c.c.	5 c.c.	...
	5 c.c.	54 c.c.	7 c.c.	50 c.c.	6 c.c.	27 c.c.	42 c.c.

Distillation in a vacuum.[1]—Liquids boiling at a high temperature under the ordinary pressure are usually distilled under diminished pressure in order that the frequent decomposition which takes place at the higher temperature may be avoided.

The simplest form of apparatus for distilling in a partial vacuum is a combination of two distilling flasks (fig. 5).

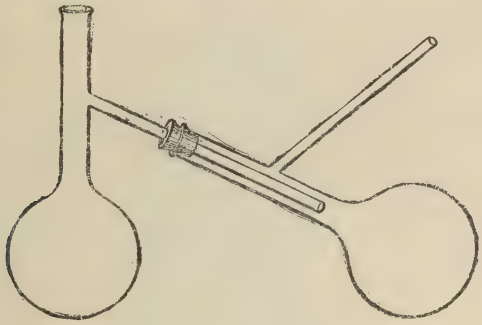


FIG. 5.

The side-tube of the flask forming the receiver is connected with the pump, and a thermometer is fitted into the neck of the other flask.

To prevent bumping a small piece of porous porcelain is put into the liquid.

As a good deal of foaming takes place when distilling under reduced pressure, the flask is filled only one-half to one-third full with the liquid.

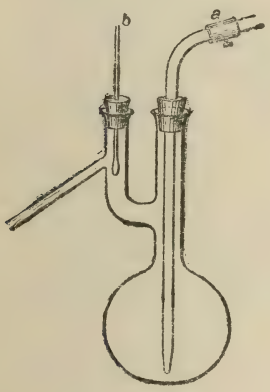


FIG. 6.

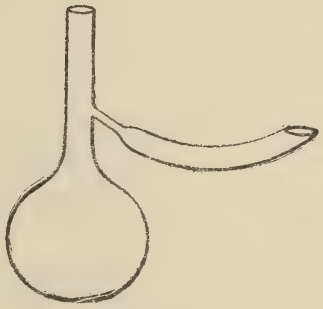


FIG. 7.

Another form of distilling flask is the Claisen flask (fig. 6). The thermometer is inserted in *b*, and a tube drawn out to a capillary point is fitted in *a* by means of a cork. The open end of this tube outside the flask is fitted with a short piece of thick-walled rubber tubing carrying a screw-clip. In carrying out a vacuum distillation in such a flask, the clip is opened slightly in order to allow a fine stream of air-bubbles to be drawn through the liquid—an arrangement which is often used to prevent irregular boiling.

For the distillation of solids a flask fitted with a wide curved tube is used (fig. 7).

[1] *Die Destillation unter vermindertem Druck im Laboratorium*, Anschütz.

In order to observe the pressure in the distillation apparatus a manometer is inserted at a convenient point (fig. 8). The difference in height between the two mercury columns gives the pressure. The complete apparatus for distilling in vacuum is shown in fig. 9.

The distilling apparatus is best put together with rubber corks. Ordinary

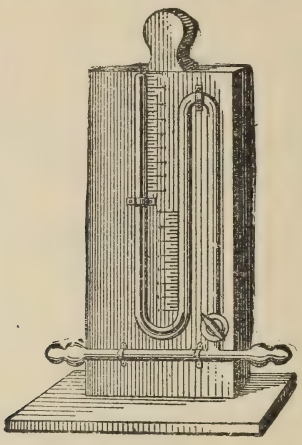


FIG. 8.

corks, however, may be made quite tight by coating them when in position with collodion. The flask, which should not be of more than 250 c.c. capacity, is best heated by either a metallic air-bath (iron crucible) or a metal bath. The lowering of the boiling-point by a reduction of pressure to about 10–20 mm. is roughly about 100° for most substances.

Distillation with steam.—In many cases where a direct distillation

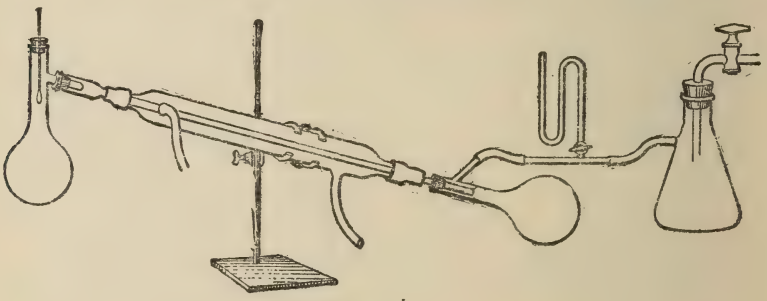


FIG. 9.

cannot be carried out, and particularly for the separation of organic from inorganic substances, distillation in a current of steam is resorted to (see *Preparation of Aniline*).

The apparatus used is shown in fig. 10.

A large tin is fitted with a two-holed stopper, through which pass a short bent delivery-tube and a long straight tube reaching to the bottom, which acts as a safety tube.

This is heated by a large burner, preferably a low "Fletcher burner." The substance to be distilled is placed in a large flask inclined as shown, in order to avoid any splashing over of the contents into the condenser. The flask is

supported on a sand-bath and heated to boiling. When the steam begins to issue from the tin, the rubber tube is slipped on to the tube reaching to the bottom of the flask, and passed through the latter till the product has been driven over. During this process the flask is not directly heated. When the distillation is finished, the rubber tube between the tin and the flask is disconnected before turning off the gas.

In some cases it is necessary to superheat the steam before passing it into the flask (*e.g.* in the distillation of α-naphthylamine). This is done by passing the steam through a copper coil heated by a large burner.

Filtration.—Most of the filtering in a technical laboratory is done with the use of a Büchner porcelain funnel, fitting, by means of a rubber stopper, into a stout filter-flask with side-tube. This is connected by "pump tubing" to the filter-pump, so that a good vacuum is produced in the flask.

The filter-paper used is that specially made for the purpose, which can be obtained in sizes suitable for any porcelain funnel (Schleicher and Schüll's No. 595 hardened filter-paper). Before use, it is moistened with water and fitted

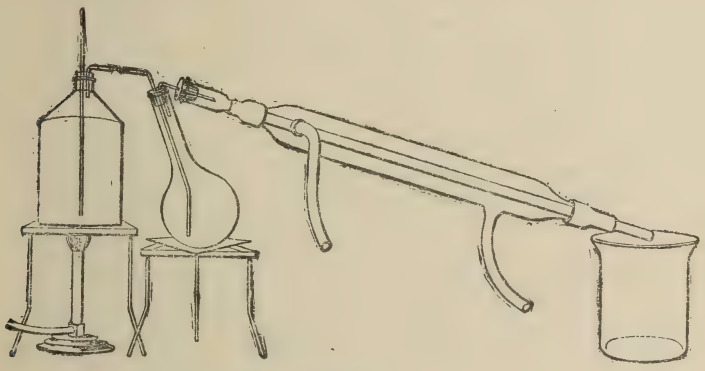


Fig. 10.

in the funnel with the pump working, in order that any crevices may be detected, and the paper pressed down round the edge with the finger.

If the paper be carefully removed after use, it may be washed with cold water and used several times. Care is taken always to disconnect the rubber tubing before turning off the water, otherwise the latter may be sucked into the flask.

In cases where a large bulk of material has to be filtered, or the precipitate filters badly under suction, the filter-cloth is used instead of paper. For the laboratory, thin, closely woven "grey cloth" (unbleached) is used. It is cut into squares about 12 inches side, and fixed on a square frame of wood, with the ends projecting, by means of nails standing up at each corner. The cloth is dipped into hot water and squeezed out before use. The frame is placed over a dish of suitable size.

When larger frames are used, side 2 feet, they are conveniently fitted with legs 2 feet long, so as to stand on the floor.

When as much as possible of the liquid has drained through, the precipitate is scraped into the centre of the cloth with a spatula and the cloth carefully taken from the frame. It is now folded up like a parcel, the ends doubled over and pressed out. If the filtrate has to be kept, this is done by putting it in an ordinary book-press, which stands in a tin shallow trough, and screwing up slowly

and carefully. If the cloth bursts, the precipitate is collected and the whole wrapped up in a second cloth. A simple way, in case the filtrate is not required, is to place the folded cloth on a table and pile a few bricks on it; after a few hours the cake will be found to be pressed hard. The cake, after pressing, is removed from the cloth with a knife or spatula and dried in the usual way. The cloth is boiled out with water, and may be used over again.

Salting out.—In order to throw a substance out of solution the method of "salting out" is very often adopted in chemical work. This consists in adding either common salt or potassium chloride (or their saturated solutions) to the solution, in order to make a salt solution in which the substance is difficultly soluble. The method is specially applicable to the cases of sulphonic acids and dyestuffs.

Generally speaking, solid salt (or in certain cases potassium chloride) is gradually added to the solution and the whole well stirred. In the case of intermediate products, the salt is usually added till no more will dissolve, when the substance separates out. Dyestuffs are precipitated gradually, a drop of the liquid being placed on filter-paper after each addition of salt till the bulk of the colour is seen to have separated. Sometimes very little salt is necessary, and if added in the solid state causes a too rapid precipitation of the dyestuff, when it comes down as a tarry mass. In such a case a saturated solution of salt is used. In some cases the sodium salt is very soluble, even in a saturated salt solution; but the potassium salt is difficultly soluble. By adding potassium chloride ("waste salt") to the solution of the sodium salt, a double decomposition takes place, and the potassium salt is precipitated. A similar reaction takes place in the instance of a sulphonic acid, which forms a difficultly soluble (in salt solution) sodium salt. If common salt be added to the solution the sodium salt will be formed and precipitated, even in presence of an excess of sulphuric acid.

Care must be taken not to add too much of the precipitant, otherwise the resulting product will be of very low percentage, owing to the presence of an excess of salt. In such a case the precipitate is carefully poured off, leaving the solid salt behind, or water is added till the excess of salt is dissolved. There is not much difference between the solubility of sodium chloride in cold and hot water, as the following table shows:—

100 parts of water dissolve the following quantities of sodium chloride at the corresponding temperatures:

Temp.,	0°	14°	25°	40°	60°	80°	100°
NaCl,	35·52	35·87	36·13	36·64	37·25	38·22	39·16

100 parts of water dissolve 28·5 parts of potassium chloride at 0°, 33·4 parts at 15°, and 59 parts at 100°.

Indicators and Reagents.—Indicators.—Besides the ordinary laboratory indicators, such as litmus, phenolphthaleïn, and methyl orange, which are used chiefly in testing acids and alkalies, the following indicators, used in the form of test-papers, are very much used in technical laboratories.

1. *Congo red.*—Filter-paper stained with an aqueous solution of this dye is used instead of litmus-paper for the indication of acids, especially mineral acids. The advantage it possesses over litmus-paper is that the colour-change is far more distinct, and also by its use it is possible to distinguish between mineral acids and organic acids.

With the former a deep blue coloration is obtained, while the latter change the red colour to dark brown. The dark brown colour is probably the colour of the free dye (Congo red being the sodium salt); while the blue produced with

mineral acids is due to the formation of a compound of the acid with the dye (Schimansky, *J.C.S.*, 1900, lxxviii. 305).

The test-paper is prepared by dipping strips of filter-paper into a solution of 5 grams of the dye in 4 litres of water. After drying it is preserved in a box in the dark.

2. *Brilliant yellow.*—5 grams of this dye are dissolved in 4 litres of water and filter-paper dipped into the solution. The dried paper is preserved in the dark. It is used for the detection of alkalies, by which it is turned red. The alkali salts of phenols and naphthols give an alkaline reaction; free alkali is detected by the method given on p. 266.

3. *Starch-iodide paper.*—10 grams of starch are ground up with 100 c.c. of cold water, and the mixture poured into 1900 c.c. of hot water, and the whole boiled for a few minutes. A solution of 3–4 grams of cadmium iodide is added and filter-paper dipped into the solution. The paper must be dried in a room free from chemical fumes, especially nitrous acid, and, after drying, preserved in a tin box or glass-stoppered bottle. The solution will not keep.

The test-paper gives the well-known blue coloration with free nitrous acid, chlorine, bromine, etc.

Reagents.—Besides the usual analytical solutions, such as standard caustic soda, sulphuric acid, potassium permanganate, etc., the following are also necessary for the technical laboratory:—

Half-normal sodium nitrite.—This is the most convenient strength for analytical work such as testing amines. To prepare it, 36 grams of ordinary sodium nitrite are dissolved in water and the solution made up to 1 litre. It is standardised by means of a solution of potassium permanganate (see page 302). 2000 c.c. correspond to 1 molecule in grams of a monamine and $\frac{1}{2}$ molecule of a diamine (benzidine, etc.).

Normal aniline solution.—This is used for preparing the standard solution of diazobenzene chloride for analysis (see page 311). 93 grams of pure aniline are dissolved in 300 c.c. of conc. hydrochloric acid and water and made up to 1 litre.

25 c.c. of this solution diazotised with 50 c.c. of half-normal nitrite and made up to 250 c.c. form a decinormal solution of diazobenzene chloride.

Potassium bromate solution.—See page 315.

Besides the above it is useful to have in the laboratory stock solutions of substances which are frequently used. They are, of course, not standardised. Among these may be the following:—

Caustic soda solution (normal).—40 grams are dissolved up to 1 litre.

Sodium carbonate solution (normal).—106 grams Na_2CO_3 are dissolved up to 1 litre.

Sodium acetate solution (normal).—136 grams $NaC_2H_3O_2.3H_2O$ are dissolved up to 1 litre.

Sodium chloride solution.—A cold saturated solution is prepared, 1 litre of water to 360 grams NaCl.

Lastly, small bottles containing (1) solution of diazotised *p*-nitraniline, (2) solution of "R salt" (*β*-naphthol disulphonate of soda) mixed with sodium carbonate (of any convenient strength) should be always at hand.

All other chemicals in the laboratory which are used in technical work, such as the common acids, amines, phenols, and naphthols, and their sulphonic acids, etc., should have the strength clearly marked on the label, together with the molecular weight according to which this has been calculated, and it is very convenient to write on the label the number of c.c. (in the case of a liquid) or grams (in the case of a solid) which contain 1 molecule of the substance in grams.

A laboratory equipped as described above and practice in the various preparations to be detailed later, which will include experience of the operations just mentioned, should enable the student or works chemist to obtain a good insight into the methods of technical organic chemistry. It is evident, however, that some experience of carrying out experiments in plant similar to that used on the large scale will be of great advantage to the university or technical school student, and for the works chemist, about to transfer his operations from the sphere of grams to that of hundredweights, almost a necessity.

To this end, therefore, it is of very considerable importance that a large, lofty room should be set aside for a miniature plant, in which most of the operations can be carried out very nearly under large-scale conditions.

With pans for sulphonation, nitration, reduction, fusion with alkali, filter-presses, tubs, etc., the chemist can not only work out a process in a manner infinitely more closely related to actual manufacturing conditions, and often find out difficulties which do not present themselves in the ordinary laboratory, but he will also acquire experience in handling plant and manipulating materials by means of compressed air, gravity, etc., that will be of the greatest use to him in the works.

As a certain amount of manual labour will be necessary for such work (for example, charging pans with sulphuric acid, emptying filter-presses and vacuum filters, etc.), the size of the appliances should be such that the quantities of materials to be handled are not too great, and the sizes recommended below have been chosen with this end in view.

The laboratory should be supplied with shafting from which, by means of fast and loose pulleys, the stirrers in the pans and tubs will be driven, and, if it is self-contained, a small electric motor may supply the power. A small combined pump will provide compressed air and vacuum; and, in addition, steam, gas, and water will be required.

The following apparatus should be provided, the number of units of which will depend on the general scale on which the work has to be carried out.

Sulphonation pan.—This should be of about 5½ gallons capacity (25 litres), of cast-iron, cylindrical, with a hemispherical bottom and fitted with a cover, bolted on, carrying a cone-shaped or screw stirrer driven by a belt from the shafting. The lid should also be fitted with a thermometer pipe, a hole for charging, into which a pipe, dipping as near to the bottom of the pan as possible, can be fitted at the end of the operation in order to blow the contents by means of compressed air into a tub or other vessel, and a small pipe furnishing compressed air. This is so arranged that when the pan is under pressure the air may be released by means of a branch pipe if necessary. The pan should be heated by gas. It is conveniently mounted on a stand so that the lid is about breast-high.

At the conclusion of an operation the agitator is stopped, the blow-out pipe fixed in and connected with the pipe through which the batch has to be blown, either to the nitrating pan or into a tub, the tap on the end of this shut, and compressed air turned on. The tap on the pipe ending over the nitration pan or tub is now opened (care being taken that the batch cannot be blown elsewhere through an open tap) to allow the sulphonation mixture to be transferred. When nearly all has passed over, care must be taken to avoid splashing owing to air escaping; this is done by careful manipulation of the tap. When nothing but air escapes, the air supply is shut off and the pressure allowed to exhaust itself through the blow-out pipe. The pan may be washed out with a little sulphuric acid, and in any case it is necessary to ensure that it is completely empty; if the blow-out pipe does not fit close to the bottom it may be necessary to take off the lid and scoop out the remainder of the batch. Reflux or ordinary

condensers of lead spiral set in a bucket or other suitable vessel can easily be connected when required.

Nitration pan.—This may be of about 3½ gallons capacity (16 litres), with the same fittings as the sulphonation pan, but should be enamelled and set in a wooden vessel in which it can be cooled by water or by a mixture of ice and salt. Steam should also be supplied to this vessel.

The finished batch is blown either into a plain enamelled pan with a bottom outlet (to separate the waste acid from the nitro-compound) or into a tub where it can be reduced or where it can be diluted or neutralised prior to being run into the reducing pan.

It is convenient also to have a nitrating vessel made of earthenware, of about 4·5 gallons capacity (20 litres), which can be stirred by hand with a porcelain or earthenware stirrer when necessary.

Reduction pan.—This may be of about 5–7 gallons capacity (22–32 litres), fitted with a stirrer supported by a bridge and an outlet tap, and heated by gas. It is conveniently set up on a stage so that the product can be run by gravity into a closed iron cylindrical vessel of about 20 gallons capacity, from which it is blown by compressed air into a filter-press. Alternately the product of reduction may be filtered through a vacuum filter.

Melt pan.—This pan should be of about 3·5 gallons capacity and should have an outlet pipe at the bottom. The other fittings required are like those of the sulphonation pan except that no compressed air is required, although this may be fitted, as it is occasionally useful; the stirrer should be of simple design, and should revolve much more slowly than those described above. The pan should be arranged for gas-heating and should be of stout construction.

Autoclaves.—One of about 2 gallons and one of about 5·5 gallons capacity should be provided. They should be tested to 100 atmospheres pressure (about 45 atmospheres pressure is reached when heating with ammonia) and be fitted with stirrer (useful, but not absolutely necessary), thermometer pipe, gauge, and release valve. They are conveniently heated by gas. Linings or "insets" of special acid-proof metal (tantiron, narki, duriron, etc.) should be provided for use with acids.

Still.—A copper still, steam-jacketed, of 6·5–11 gallons capacity, for distilling alcoholic or toluene solutions is useful, as is also a similar one fitted with a fractionating column for rectifying alcohol or benzene.

Vacuum still.—A copper still of about 2 gallons capacity, provided with two receivers, each with bottom outlet, is useful for distilling solids. The receivers are connected to the vacuum and, together with the condenser, can be kept hot by means of small gas jets to prevent the distillate solidifying.

Tubs.—Several of these should be provided. They may be of 20–30 gallons capacity, made of pitch pine, and fitted with stirrers of the same wood and bottom outlet. They are conveniently arranged in sets of two or three, one above the other, and should be provided with a water supply and a steam-pipe.

Filter-press.—Two at least of these (of wood) should be provided for one unit. Their capacity should be such that when a sulphonation mixture has been neutralised with milk of lime in one of the tubs, the whole of the calcium sulphate may be contained in one press. They should be fitted with water and steam for washing the cakes, and with compressed air for blowing the cakes dry. Woollen cloth should be used for filtering acid liquids, and cotton for neutral or alkaline ones.

Vacuum filters.—Two at least of these are necessary. The filtering surface should be about 100 sq. inches. They are conveniently constructed of acid-proof metal or of cast iron, lead-lined, and should be connected with a lead-lined receiver of about 20 gallons capacity.

Receivers.—Two of these should be provided of 20–30 gallons capacity. They are closed cylindrical iron vessels, into which the (neutral or alkaline) contents of a tub or a reduction pan can be run, and are thence blown through a filter-press or where required.

In addition to the above there should be provided a hand-press (such as is used for copying letters) for pressing out precipitates when necessary, a centrifuge about 18 inches in diameter, a steam-jacketed evaporating pan, a small vacuum drying oven, a mechanically-driven pestle and mortar, a ball-mill (about 16 inches wide) for grinding dyes, scale to weigh from 1 oz. to 100 lbs., and various enamelled pans (5–10 gallons capacity), wooden buckets, earthenware jugs for acids, etc.

It is convenient to store carboys of acids and kegs of materials in a room adjoining the laboratory, where may also be placed a bench at which a mechanic in attendance can carry out small repairs, pipe-fitting, etc.

CHAPTER XXVII.

PREPARATIONS OF INTERMEDIATE PRODUCTS.

Introductory.

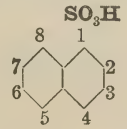
The principal operations which are carried out on the large scale in the preparation of the raw materials for the production of dyestuffs are the following :—

1. *Sulphonation;* introduction of the group SO_3H.[1]
2. *Nitration and reduction;* introduction of the groups NO_2 and NH_2.
3. *Diazotisation and subsequent boiling with water;* conversion of the NH_2 group into the OH group.
4. *Conversion of the* NH_2 *group into the* OH *group* by boiling with dilute acids or alkalies.
5. *Fusion of the* SO_3H *group with caustic alkali;* forming the OH group.
6. *Conversion of the* OH *group into the* NH_2 *group* by treatment with ammonia.
7. *Molecular rearrangement of the* SO_3H *group* by heat.
8. *The elimination of the* SO_3H *group* by treatment with acids, etc.

Examples of these processes and a description of them will be found in the following pages.

Conversion of the NH_2 group into the OH group by boiling with dilute acids or alkalies.—This is an operation very frequently carried out on the large scale, and is particularly applicable to the case of the amido- or diamidonaphthalene sulphonic acids.

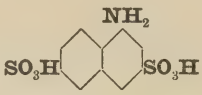
[1] In the naphthalene series this group never enters into the *ortho-*, *para-*, or *peri*-position with regard to a sulphonic acid group already in the α-position, *i.e.*



on further sulphonation never gives a 1 : 2, 1 : 4, or 1 : 8 disulphonic acid ; and if the first SO_3H group is in a β-position, the second never enters into the corresponding ortho-position, *i.e.* a 1 : 2-disulphonic acid is never obtained. See also *Chem. Zeit.*, 1893, 758 ; 1894, 180 ; *Proc. C.S.*, 1890, 130 ; *Ber.*, 1894, xxvii. 1209 ; and p. 11 of this book.

The process in many instances is carried out by heating with water alone, of course under pressure.

Thus by heating a mixture of the acid of formula

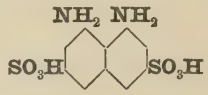


and three parts of water to 180°, the corresponding α-naphthol disulphonic acid is formed.

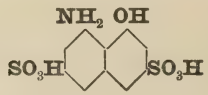
It is usual, however, to employ dilute hydrochloric or sulphuric acid.

When two amido-groups are present, the reaction may be so modified by the regulation of the temperature that only one NH_2 group is converted into OH, the second being changed at a higher temperature.

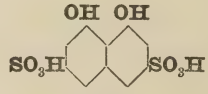
Thus the acid of the formula



on heating with water, dilute acids, or dilute alkalies, gives first

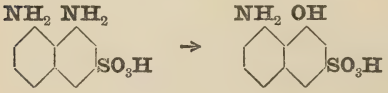


(H acid), and at a higher temperature



(chromotropic acid).

When the diamido-acid is asymmetric, the NH_2 group nearest to the sulphonic acid group is the first to be converted; thus:—



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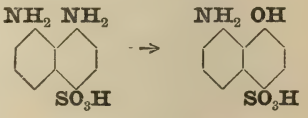
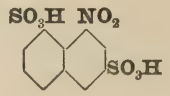


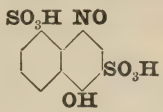
In a few cases alkalies, such as milk of lime or dilute caustic soda, are used.

With regard to the use of *dilute caustic soda*, an interesting example may be here mentioned, although it is not concerned with the conversion of the NH_2 group into the OH group.

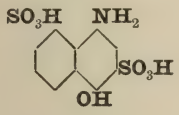
If a *nitro*-acid be treated with caustic soda, an hydroxyl group is introduced into the nucleus, the oxygen being supplied by the nitro-group, which is reduced to the nitroso-group. Thus



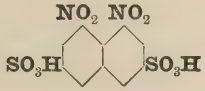
on being boiled with caustic soda solution, yields



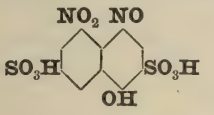
which, on reduction, yields



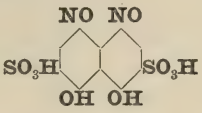
; and the acid



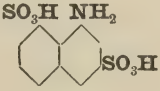
yields, on treatment with alkalies in the cold, first



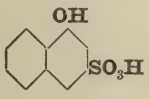
and then



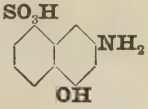
Elimination of the SO_3H group by treatment with dilute acids, etc.—By heating a sulphonic acid with water or dilute acids, the SO_3H group is often entirely eliminated. If an amido-group is present, this is sometimes changed into the hydroxyl group at the same time; thus the acid having the formula



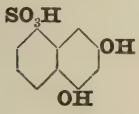
yields a naphthol sulphonic acid of formula



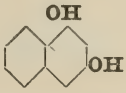
; and the acid



gives, first,



and then



(naphthoresorcinol).

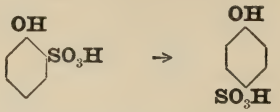
As a rule, stronger acid (50 per cent. sulphuric acid) and sometimes a higher temperature is necessary to split off the SO_3H group than is required for the change of NH_2 to OH.

In a polysulphonic acid the SO_3H group in an α-position is eliminated before one in the more stable β-position.

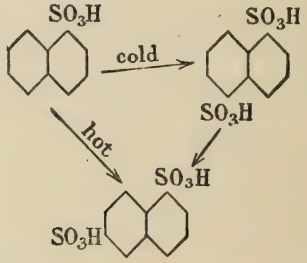
(For an example of the necessity of such elimination of the SO_3H group after its introduction at an earlier stage, see *Ethoxybenzidine*, p. 22.)

Molecular rearrangement of the SO_3H group.—The transference of this group from one position to another in the benzene or naphthalene ring is brought about by the action of heat. That is to say, if the group has been already introduced into a molecule, it may be driven from its position by raising the temperature; and, further, if a second group, either the same or a different one, be present in the molecule, the second position taken by the SO_3H group will be as far as possible away from the other group. Thus in the benzene series, if phenol be sulphonated in the cold, the *ortho*-sulphonic acid is formed; but if

the temperature be slightly raised, the sulphonic acid group migrates to the *para*-position; thus:—

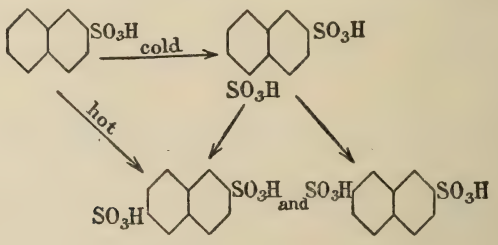


In the naphthalene series there are many striking examples of this molecular rearrangement. Thus naphthalene itself, on treatment with sulphuric acid at a low temperature, forms naphthalene-α-sulphonic acid; but if the temperature be raised, the β-compound results. The general tendency in the naphthalene series is for the sulphonic acid group to migrate in the first instance from an *alpha*-position to a *beta*-position (when the temperature is raised); and, when the other group in the molecule is an SO_3H group, any further migration results in a compound having these groups as widely separated from each other as possible, the β-position being, however, always preferred. Thus naphthalene-α-sulphonic acid, on further sulphonation, gives the following:—



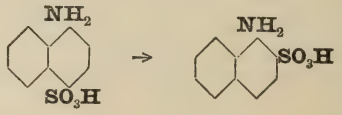
The formation of the latter acid at a higher temperature is regarded as having been preceded by the initial formation of the 1 : 5 acid, which undergoes molecular change in the direction indicated, at a higher temperature.

Further, on sulphonating naphthalene-β-sulphonic acid we obtain



in a similar way.

An interesting case of molecular change where an excess of sulphuric acid is not present is that undergone by naphthionic acid. If this substance be heated with two to three parts of naphthalene to the boiling-point of the latter (217°), the SO_3H group migrates from the α-position to the β-position; thus:—



It is worthy of remark, however, that this latter acid is not formed at all by the sulphonation of α-naphthylamine, but, up to a certain temperature, naphthionic acid is the sole product.

Similar cases to those cited above occur in the case of the β-naphthol sulphonic acids.

If β-naphthol be sulphonated at a low temperature, we obtain the 2 : 8-acid, but at a high temperature this passes into the 2 : 6-acid. (See also the description of the other β-naphthol sulphonic acids, especially the disulphonic acids R and G on p. 16.)

I. BENZENE SERIES.

1. *Nitrobenzene*, $C_6H_5NO_2$.

50 grams benzene.
60 „ conc. nitric acid, sp. gr. 1·4 (43 c.c.).
90 „ conc. sulphuric acid (50 c.c.).

The nitric acid is added in small portions at a time to the sulphuric acid contained in a small flask. During this process the flask is well cooled under the tap. The mixture is transferred to a tap-funnel and added slowly to the benzene in a half-litre flask. The flask is well shaken and cooled after each addition, and the temperature must not be allowed to rise above 25° until nearly all the acid has been added, when it may reach 50°. A wide glass tube is now attached by a cork to the flask, forming a vertical air-condenser, and the nitration mixture is heated in a water-bath (water at 60°) for one hour, being frequently shaken. The contents of the flask are poured into about 1 litre of water, when the nitrobenzene sinks to the bottom. If the settling is not at once complete, the mixture is allowed to stand for some time. A large portion of the acid solution may be decanted, and the rest, together with the nitrobenzene, is transferred to a separating funnel and the nitrobenzene drawn off, the top layer of acid being thrown away. The former is again transferred to the funnel, three or four times its bulk of water added, the whole shaken, and, after settling, the oil again drawn off. This operation is repeated once more, after which the nitrobenzene is run into a distilling flask of about 300–400-c.c. capacity, which is then fitted with a thermometer and connected with a long glass tube about 8–10 mm. in diameter, forming an air-condenser. The oil is distilled over the free flame.

At first water and benzene pass over, then the temperature rises rapidly to over 200°, when the receiver is changed and the nitrobenzene collected at 204–207°. Yield 55–60 grams. The yield obtained on the large scale corresponds to 75 grams. The difference is accounted for by the fact that, on the large scale, the stirring is continuous and no nitrobenzene is lost in the wash-waters. Any benzene, also, which is recovered by distillation is nitrated with the next batch.

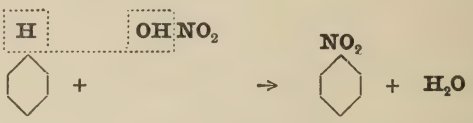
Properties.—Light yellow liquid, with a smell of bitter almonds; B.P. 206–207°, M.P. 3°, sp. gr. at 15° = 1·208. Nitrobenzene comes on the market as (1) light or pure nitrobenzene, B.P. 205–210°, sp. gr. 1·2; and (2) heavy

nitrobenzene (containing nitrotoluenes), B.P. 210–220°, sp. gr. 1·18. The terms "light" and "heavy" apply, not to the specific gravities, but to the boiling-points.

Commercial nitrobenzene is tested by determining (1) the boiling-point and (2) the specific gravity.

Use.—Pure nitrobenzene is used for the manufacture of aniline, benzidine, and in perfumery. Heavy nitrobenzene is used in the manufacture of Magenta.

Equation.—



The sulphuric acid acts as a dehydrating agent.

2. *Aniline.*

100 grams nitrobenzene.
120 „ iron powder.
10 „ conc. hydrochloric acid.

The reduction of nitrobenzene, as well as other nitro-bodies, is carried out on the large scale by the use of iron borings. This cannot be satisfactorily imitated in the laboratory; consequently it is usual to reduce nitrobenzene on the small scale by means of tin and hydrochloric acid. If, however, very finely divided iron or "iron powder" be used, the reduction proceeds very smoothly, and a yield equal to that given by the former method is easily obtained.

The iron, together with 160 c.c. water, is placed in a large flask of 2–3-litres capacity and well shaken. The flask is now warmed slightly, and a few drops of nitrobenzene added. Then the acid is poured into the flask, and the remainder of the nitrobenzene in small portions at a time. After each addition the flask is thoroughly well shaken and cooled under the tap. The addition of nitrobenzene and amount of cooling are so arranged that the temperature keeps at about 80–90°. When the reaction is finished (shown by no further rise in temperature on shaking), the contents of the flask are distilled with steam (it is not necessary to make the mixture alkaline) till the distillate is no longer milky. The volume of this will be about 400–500 c.c. The distillate is transferred to a separating funnel, allowed to settle (if necessary), and the aniline, which forms the lower layer, drawn off. The water (which, on the large scale, is returned to the steam boiler, as it contains about 3 per cent. of aniline in solution) is now saturated with common salt and allowed to stand for some time. The aniline, which rises to the top, is separated by means of a separating funnel, added to the first portion of oil, and the whole distilled. A little water passes over at first and is separately collected; the aniline then passes over at 182°. Yield 50–70 grams.

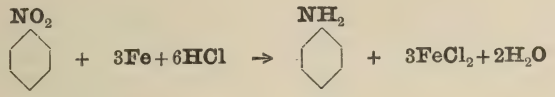
Properties.—Colourless oil with a peculiar smell; B.P. 182°, sp. gr. 1·026 at 15°.

Commercial "pure aniline" is tested by distillation. At least 90 per cent. by volume should distil at 182°. It should give a clear solution with hydrochloric acid; a yellow colour indicates the presence of nitrobenzene.

"Aniline for red" (*i.e.* for the manufacture of Magenta) is a mixture of aniline (35 to 42 per cent.), orthotoluidine (35 to 50 per cent.), and paratoluidine (14 to 24 per cent.). It results from the reduction of "heavy nitrobenzene." It should boil between 190° and 200°, and have a specific gravity of 1·007 to 1·009 at 15°.

Use.—Aniline is used for making a large number of its substitution products, as well as for Quinoline, Induline, Magenta, Aniline blue, diazobenzene salts (for azo-dyes), and Aniline black.

Equations.—



(See also p. 20.)

3. *Acetanilide.*

Walter, *Aus der Praxis der Anilinfarbenfabrikation*, 1903.
Müller, *Chem. Zeit.*, 1912, xxiv. 1055.

200 grams aniline.
150 „ glacial acetic acid.

The aniline and acetic acid are mixed in a round flask of one-litre capacity, fitted with an air-condenser, and boiled on a sand-bath for ten to twelve hours. The tube forming the air-condenser should not be too long, in order that the water vapour may escape while the aniline and acetic acid are condensed.

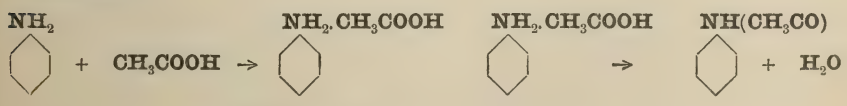
The hot liquid is poured into hot water containing 30 grams of concentrated hydrochloric acid, and the whole well stirred. After cooling, the acetanilide is filtered at the pump and washed with water. The filtrate contains about 20–30 grams of aniline as hydrochloride, which, on the large scale, is regained.

The acetanilide is transferred to a porcelain dish and dried at 110–120°. On cooling, the solidified product is broken up and powdered in a mill. Yield 220–250 grams.

Properties.—Acetanilide is difficultly soluble in cold, more easily soluble in hot water, from which it crystallises in white leafy crystals; M.P. 115°, B.P. 295°. By boiling with concentrated hydrochloric acid, it is hydrolysed to aniline and acetic acid.

Use.—Acetanilide is used largely for the preparation of *p*-nitraniline.

Equation.—



(aniline acetate).

4. *p-Nitracetanilide.*

Walter, *loc. cit.*; Müller, *loc. cit.*

100 grams acetanilide.
300 „ conc. sulphuric acid (167 c.c.).
62·5 „ conc. nitric acid (44 c.c.).
50 „ conc. sulphuric acid (28 c.c.).

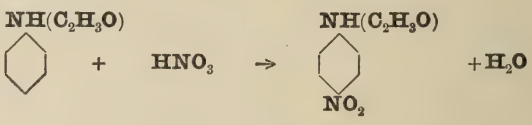
The acetanilide is dissolved in 300 grams of sulphuric acid contained in a round flask, the temperature not being allowed to rise above 40°. The solution is cooled to 5–10° by immersion in ice-water, and the cooled mixture of 62·5 grams of nitric acid with 50 grams of sulphuric acid is added very slowly. After each addition the flask is well shaken and cooled in the ice-water, the temperature being kept below 15°. After standing a short time, the nitration mixture is poured into about 10 litres of water containing several lumps of ice, when the *p*-nitracetanilide separates out, and is filtered, washed free from acid, and dried on a porous plate. Yield 110–120 grams.

Properties.—*p*-Nitracetanilide crystallises from alcohol in almost colourless needles; M.P. 207°.

The presence of orthonitracetanilide is detected by extracting with chloroform, in which the *o*-compound is soluble. The technical product should give the calculated amount of *p*-nitraniline on boiling with hydrochloric acid, which is tested by titration with standard solution of sodium nitrite.

Use.—*p*-Nitracetanilide is used for the preparation of *p*-nitraniline[1] and *p*-amidoacetanilide.

Equation.—



5. *p-Nitraniline.*

100 grams *p*-nitracetanilide.

The acetyl compound is boiled with 250 c.c. of dilute sulphuric acid (25 per cent.) in a round flask attached to a reflux condenser until the whole dissolves. The clear solution is poured into a beaker, and the free base precipitated by adding dilute caustic soda solution till alkaline. After cooling, the *p*-nitraniline is filtered, recrystallised from hot water (on the large scale this is done under pressure), and dried on a porous plate. Yield 70–75 grams.

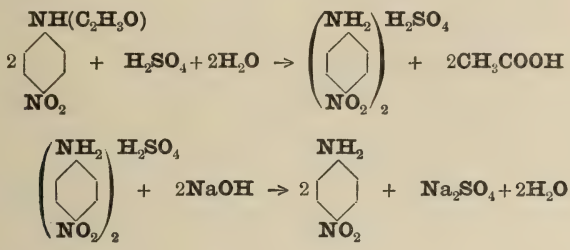
Properties.—Yellow needles or prisms; M.P. 147°; dissolves in 1250 parts of water at 18°; not volatile with steam. The commercial product should be a light

[1] For the manufacture of *p*-nitraniline see Müller, *Chem. Zeit.*, 1912, xxxvi. 1055.

yellow powder, having the correct melting-point, and dissolving without residue in hydrochloric acid. It is tested by titration with standard sodium nitrite solution. For details of diazotisation, see p. 264.

Use.—*p*-Nitraniline is used in the production of azo-dyes, and also for the preparation of its diazo-compound, which, by combination with β-naphthol on the fibre, yields paranitraniline red.

Equations.—



6. *p-Amidoacetanilide.*

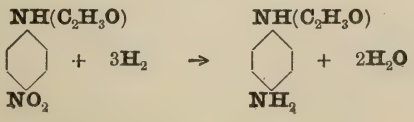
Nietzki, *Ber.*, 1884, xvii. 343.

100 grams *p*-nitracetanilide.
100 „ iron powder.
20 „ acetic acid, 30 per cent.

The iron and acetic acid are placed in a round flask, together with 300 c.c. of water, and about half of the nitracetanilide is added. The flask is well shaken and gradually becomes warmer as the reduction proceeds. The rest of the nitro-compound is gradually added, and the temperature is not allowed to rise above 80°. The end of the reaction is reached when the contents of the flask lose their yellow colour and the temperature, after shaking, falls. Sodium carbonate solution is then added till an alkaline reaction is obtained, and the mixture filtered hot at the pump. The residue is boiled up several times with water and filtered again. The united filtrates are saturated with salt, and on cooling fine needle-shaped crystals of amidoacetanilide separate out. They are filtered, and dried on a porous plate. Yield 50–60 grams. On the large scale, amidoacetanilide is purified by distillation *in vacuo* (in which form it is sold), or the reduction liquor is diazotised direct for the production of azo-colours (direct cotton blacks).

Properties.—M.P. 161°. Analysis: with half-normal sodium nitrite solution.

Equation.—



7. *p-Sulphanilic acid.*

Nevile and Winther, *Ber.*, 1880, xiii. 1940.
Mühlhäuser, *Ding. pol. J.*, 1887, cclxiv. 181, 238.
Paul, *Zeit. ang. Chem.*, 1896, 685.

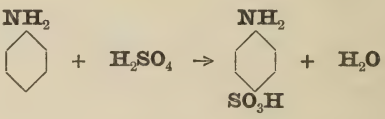
100 grams aniline.
110 „ conc. sulphuric acid (61 c.c.).

The aniline is stirred into the acid contained in a shallow porcelain basin, and the acid sulphate thus obtained ($C_6H_5NH_2.H_2SO_4$) is heated in an oven till the temperature reaches 205°. This must take four hours. The oven is kept at this temperature for six hours more. The product is broken up and dissolved in hot water with addition of 40 grams of caustic soda. (An alkaline reaction must be obtained.) The solution of sodium sulphanilate is boiled for a few minutes with a little animal charcoal and filtered hot. On acidifying with hydrochloric acid (Congo paper must be turned blue) the sulphanilic acid crystallises out; after standing overnight it is filtered at the pump and dried at 100°. Yield 150–160 grams.

Properties.—Sulphanilic acid crystallises from water in large colourless plates containing one molecule of water of crystallisation, which, however, is easily driven off. It is sparingly soluble in cold, more easily in hot water. The technical product, which is not purified on the large scale, is usually dark grey. It should dissolve in alkalies, giving a clear solution containing only a trace of black insoluble matter. The strength is determined by titration with standard sodium nitrite solution.

Use.—Sulphanilic acid is used largely in the preparation of azo-dyes.

Equation.—



8. *Dimethylaniline.*[1]

Schoop, *Chem. Zeitung*, 1887, 253; *J. Soc. Chem. Ind.*, 1887, 436.

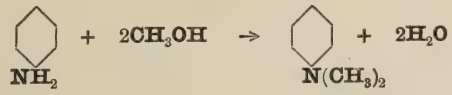
75 grams aniline.
25 „ aniline hydrochloride.
75 „ methyl alcohol.

The mixture is heated in an autoclave for seven to eight hours to 230–240°, the product then made alkaline with NaOH, distilled with steam, and the oil separated with a separating funnel. It is dried with solid caustic potash and fractionated.

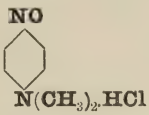
[1] For the manufacture of dimethylaniline see Walter, *Chem. Zeit.*, 1910, xxxiv. 641.

The fraction boiling at 190–200° is collected.
Properties.—Mobile liquid; B.P. 192°.

Equation.—



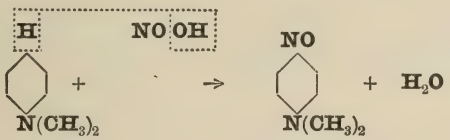
9. *Nitrosodimethylaniline hydrochloride.*



100 grams dimethylaniline.
400 „ conc. hydrochloric acid (345 c.c.).
60 „ sodium nitrite.

The dimethylaniline is dissolved in the hydrochloric acid, and ice added till the temperature sinks below 0°. The sodium nitrite, dissolved in a small quantity of water, is slowly added, the whole being stirred mechanically and the temperature not being allowed to rise above 8°. The hydrochloride of nitrosodimethylaniline separates out, and, after standing, is filtered at the pump, washed with a little dilute hydrochloric acid, and dried on a porous plate.
Properties.—Yellow needles; M.P. 177°.

Equation.—



(nitrosodimethylaniline (base)).

10. *Diethyl-m-amidophenol.*

A.P. 403,678; D.P. 44,792[88].

Wolfrum, *Chemisches Praktikum*, Pt. II. 326.

50 grams diethylaniline.
150 „ fuming sulphuric acid, 30 per cent. SO_3.

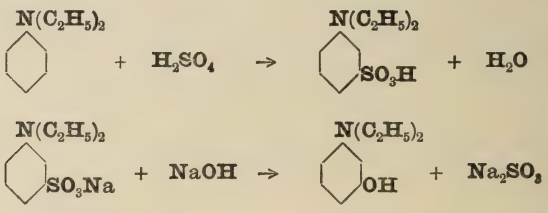
The acid is placed in a 500-c.c. round flask (fitted with a reflux condenser) and heated on a boiling-water bath. The diethylaniline is added drop by drop during half an hour. The heating is continued till a sample, rendered alkaline and extracted with ether, gives no residue of diethylaniline after evaporation

of the ether. The product is then allowed to cool, poured into 1 litre of water, and nearly neutralised with milk of lime, the complete neutralisation being effected by the addition of chalk till this produces no more effervescence. The calcium sulphate is filtered off, washed well, and sodium carbonate added to the filtrate till no further precipitate is produced; the precipitate is filtered, and the solution of the sodium salt evaporated to dryness, first over the free flame and finally on the water-bath. The sodium salt of the diethylaniline meta-sulphonic acid is now converted into the phenol by fusion with caustic soda. The fusion is done in a nickel crucible of 250-c.c. capacity, which is heated in an oil-bath. One part of the dry sodium salt is added gradually to a mixture of one part of caustic soda and one-third of a part of water, which is heated to 260–270°. During the addition of the sodium salt the contents of the crucible are well stirred by a thermometer encased in a copper tube. Gloves and spectacles must be worn to avoid accidents due to spirting.

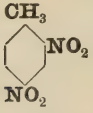
When all the sodium salt has been added the temperature is maintained at 270° for five minutes and the mass allowed to cool. The contents of the crucible are, when cold, extracted several times with water acidified with hydrochloric acid, and the neutralised solution evaporated to a small bulk, when the diethylamidophenol crystallises out. This is filtered at the pump and dried on a porous plate.

Properties.—M.P. 78°, B.P. 275–280°; is used for the preparation of Rhodamine B (p. 280).

Equations.—



11. *m-Dinitrotoluene.*



Kayser, *Zeit. Farb. Chem.*, 1903, ii. 16, 32.

100 grams toluene.

First nitrating acid	175	„	conc. sulphuric acid (98 c.c.).
	113	„	conc. nitric acid, sp. gr. 1·45 (78 c.c.).
Second nitrating acid	338	„	conc. sulphuric acid (188 c.c.).
	113	„	fuming nitric acid, sp. gr. 1·5 (76 c.c.).

The toluene is placed in a stout round flask of about one-litre capacity, which is fitted with a three-holed rubber stopper, carrying (1) a thermometer reaching nearly to the bottom of the flask, (2) a small funnel, and (3) a glass tube bent at right angles to carry off the fumes. The first mixture of "nitrating acid" is added through the funnel in small portions at a time, the flask being well

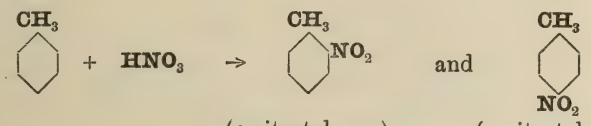
shaken after each addition and the temperature being kept at 60°. When all the acid has been added, the temperature is kept at 60° for half an hour, and the flask well shaken, then allowed to cool. The contents are now transferred to a separating funnel and the acid drawn off. The oil (a mixture of *o*- and *p*-nitrotoluene) is put back into the flask, and the second "nitrating acid" added slowly. The temperature rises and is kept at 115°, if necessary, by warming on the water-bath. After the whole of the acid has been added, the flask is kept hot and shaken for one hour at frequent intervals. The contents of the flask are now allowed to cool somewhat by standing for fifteen minutes, and poured, while still hot, into a glass funnel, which has been temporarily converted into a separating funnel by means of a thick glass rod (or a glass rod fixed to a small stopper), which closes the opening from the top. If an ordinary tap-funnel is used the hot liquid is apt to crack the stopper. The acid is drawn off and the oil is run into a litre of boiling water, and the whole stirred up. Most of the water is poured off, and the last traces of water are separated by the use of the glass funnel previously warmed with hot water. The liquid dinitrotoluene is allowed to crystallise in a dry basin. The yield is 165 grams. The nitrating acid, on cooling, deposits a further quantity of dinitrotoluene as crystals (about 12 grams), which are filtered, melted in boiling water, and separated as before.

Properties.—Long yellow needles; M.P. 71°.

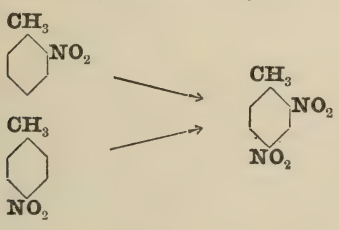
The commercial product should be light-coloured and not contain oil. The melting-point should be nearly correct.

Use.—*m*-Dinitrotoluene is used mostly in the preparation of *m*-toluylenediamine.

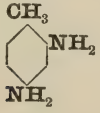
Equations.—

(1) 

(*o*-nitrotoluene) (*p*-nitrotoluene).

(2) 

12. *m-Toluylenediamine.*



100 grams *m*-dinitrotoluene.
8 „ conc. hydrochloric acid.
225 „ iron powder.

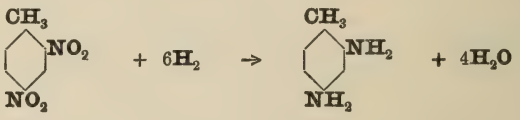
The iron powder is placed in a round flask together with 300 c.c. of water and a little *m*-dinitrotoluene. The acid is now added and the mixture well

shaken; a little more dinitrotoluene is added, and the flask heated to 60–70°, if necessary, in order to start the reaction. The nitro-compound is added gradually, in small portions at a time; the temperature rises after each addition, and the next portion is not added until the temperature begins to fall. This should not be allowed to rise over 80°, the flask being cooled, if necessary, under the tap. When the reduction is finished, the mixture is filtered hot at the pump, the iron residue transferred to the flask, and boiled up with water and filtered again. The united filtrates are allowed to cool, when the *m*-toluylenediamine crystallises out in fine white needles. These are filtered off, and the filtrate further concentrated, when a second crop of crystals is obtained. If a solution only of *m*-toluylenediamine is required, the filtrates may be diluted and tested by standard solution of diazobenzene chloride (see p. 311) in presence of sodium acetate.

Properties.—Colourless needles soluble in hot water, alcohol, and ether; M.P. 99°, B.P. 283–285°.

Use.—*m*-Toluylenediamine is used in the manufacture of Bismarck brown, many Cotton blacks, and as a "Developer."

Equation.—



13. *Benzidine.*

Erdmann, *Zeit. ang. Chem.*, 1893, 163.

100 grams nitrobenzene.
170 „ zinc dust.
105 „ caustic soda.

The caustic soda is dissolved in 300 c.c. of water, 50 c.c. of methylated spirit, and the nitrobenzene added, the operation being carried on in a round flask of 1½–2-litres capacity. The flask is fitted with a cork, through which passes a glass tube about 2 inches long, by means of which connection is made with a reflux condenser by using a 6-inch length of ¼-inch rubber tubing. The zinc dust, which must have been passed through a fine sieve, is now added in small portions at a time to the mixture, and it is essential that the flask should be thoroughly well shaken after each addition of zinc, and, indeed, throughout the experiment. The zinc dust produces a vigorous reaction and the mixture boils. The mixture is kept boiling by successive additions of zinc, but this should not be added so quickly as to cause the contents of the flask to foam up.

The brown colour gradually disappears, and when the reduction is complete the contents of the flask should appear greyish white. If this effect is not produced at this stage, more zinc dust may be added, and the flask heated on the sand-bath till reduction is complete. The contents of the flask are cooled, diluted with water, ice added, and the whole carefully acidified with hydrochloric acid, the temperature not being allowed to rise above 15°.

The hydrazobenzene separates out in crusts, which are easily separated from the liquid, and any zinc remaining undissolved, by pouring the whole

through a porcelain funnel (without paper), and washing the hydrazobenzene with water.

This is now converted into benzidine by covering it with cold concentrated hydrochloric acid and, after about half an hour, diluting with water, boiling, and filtering the solution of benzidine hydrochloride. To the filtrate sodium sulphate is added, to precipitate the benzidine as sulphate. This is filtered, washed, and boiled with dilute caustic soda solution. The solution of the free base is filtered, and the benzidine crystallises out on cooling, is filtered, and dried on a porous plate.[1] Yield 20–30 grams.

Properties.—Benzidine crystallises from hot water in large silky plates; M.P. 127·5–128°. It is tested by titration with standard sodium nitrite solution.

Use.—Benzidine is used for the preparation of direct-dyeing cotton colours.

Equations.—

(1) $\begin{matrix}C_6H_5NO_2\\C_6H_5NO_2\end{matrix} + 3H_2 \rightarrow \begin{matrix}C_6H_5N\\|\ \ O\\C_6H_5N\end{matrix} + 3H_2O$

(azoxybenzene).

(2) $\begin{matrix}C_6H_5N\\|\ \ O\\C_6H_5N\end{matrix} + H_2 \rightarrow \begin{matrix}C_6H_5N\\\|\\C_6H_5N\end{matrix} + H_2O$

(azobenzene).

(3) $\begin{matrix}C_6H_5N\\\|\\C_6H_5N\end{matrix} + H_2 \rightarrow \begin{matrix}C_6H_5NH\\|\\C_6H_5NH\end{matrix}$

(hydrazobenzene).

(4) $\begin{matrix}C_6H_5NH\\|\\C_6H_5NH\end{matrix} \xrightarrow{\text{by molecular change}} \begin{matrix}C_6H_4NH_2\\|\\C_6H_4NH_2\end{matrix}$

(benzidine).

14. *Thiocarbanilide* (*sym. Diphenylthiourea*).

$CS(NHC_6H_5)_2$

200 grams aniline.
200 ,, carbon bisulphide.
200 ,, absolute alcohol.

The aniline, carbon bisulphide (great care to be taken not to bring this in the neighbourhood of a flame), and alcohol are mixed together in a round flask fitted with a reflux condenser, and gently boiled on the water-bath for about ten hours. As sulphuretted hydrogen is evolved, an exit tube may be attached to the top of the condenser, leading either to a draught cupboard or into soda-lime. The mass solidifies after a time.

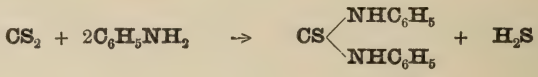
When the reaction is finished, the alcohol and excess of carbon bisulphide are distilled off on the water-bath (there must be no flame near the receiver !). Water is added, and the crystals are filtered, washed first with very dilute hydro-

[1] On the large scale, benzidine is purified by distillation *in vacuo*.

chloric acid, to remove any unchanged aniline, and finally with water. The thiocarbanilide is dried on a porous plate. Yield 200–230 grams.

Properties.—Colourless rhombic plates; M.P. 151°; used for the preparation of Indigo by Sandmeyer's method.

Equation.—



$$CS_2 + 2C_6H_5NH_2 \rightarrow CS(NHC_6H_5)_2 + H_2S$$

15. *Benzal chloride.*

$C_6H_5CHCl_2$

50 grams toluene.

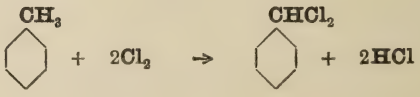
The toluene is placed in a 100-c.c. round flask with a wide neck, which is fitted with a doubly-bored stopper. Through one hole passes the tube of a reflux condenser, and through the other a narrower glass tube (reaching to the bottom of the flask), through which a current of dry chlorine is led. The flask is placed in the sunlight, the toluene heated to boiling, and a current of dry chlorine conducted into it until its weight is increased by 40 grams. (The chlorine may be conveniently prepared by warming a mixture of concentrated hydrochloric acid and powdered potassium bichromate; it is dried by bubbling through concentrated sulphuric acid). The flask and toluene are weighed before the experiment, and by weighing again after passing the current of chlorine for some time the progress of the chlorination may be observed. In summer the reaction is complete in a few hours, but in winter a much longer time may be necessary.

The reaction may be assisted by adding 4 grams of phosphorus pentachloride to the toluene. The crude product is not separated, but is used immediately for the preparation of benzaldehyde (see below).

Properties.—Colourless liquid; B.P. 206°.

Analysis.—By determining the boiling-point and, if necessary, the percentage of chlorine.

Equation.—



$$C_6H_5CH_3 + 2Cl_2 \rightarrow C_6H_5CHCl_2 + 2HCl$$

16. *Benzaldehyde.*

C_6H_5CHO

90 grams crude benzal chloride.

The crude benzal chloride is transferred to a round flask fitted with a reflux condenser, 500 c.c. of water and 150 grams of precipitated calcium carbonate added, and the mixture heated for four hours in an oil-bath (temperature of bath,

130°). (On the large scale the benzal chloride is heated with water and a salt of iron.) The contents of the flask are now distilled with steam until no more oil passes over. Before the crude benzaldehyde is purified, the liquid remaining in the flask is filtered while hot and excess of concentrated hydrochloric acid added. On cooling, the benzoic acid, which is formed as a bye-product, separates out in leafy crystals. It is filtered off and recrystallised from hot water. M.P. 121°.

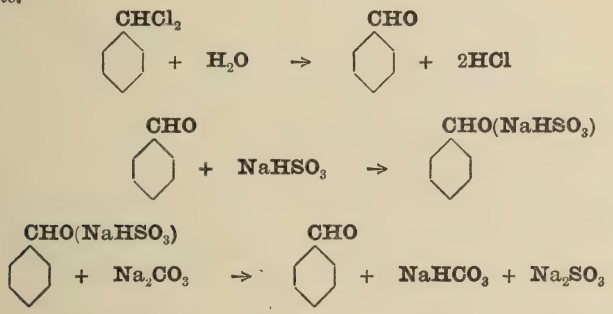
The steam distillate is now treated with a concentrated solution of bisulphite of soda ($NaHSO_3$) until, after long shaking, the greater part of the oil has passed into solution. If crystals of the double compound of benzaldehyde and sodium hydrogen sulphite separate out, water is added until they are dissolved. The aqueous solution is filtered from the oil remaining undissolved, and the filtrate treated with anhydrous sodium carbonate until an alkaline reaction is obtained. The liquid is then distilled with steam, when pure benzaldehyde passes over, and, after standing, is separated by means of a tap-funnel. It is finally distilled, preferably in a stream of hydrogen.

Properties.—Colourless liquid, smelling of bitter almonds; B.P. 179°, sp. gr. 1·0504; slightly soluble in water.

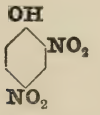
Benzaldehyde is used largely in the preparation of Malachite green; also benzoic acid and cinnamic acid.

Analysis.—(See p. 313.)

Equations.—



17. *m-Dinitrophenol.*



Engelhardt and Latschinow, *Ber.*, 1870, iii. 97.
Clemm, *J. pr. Chem.*, 1870, [2], l. 145, 170.

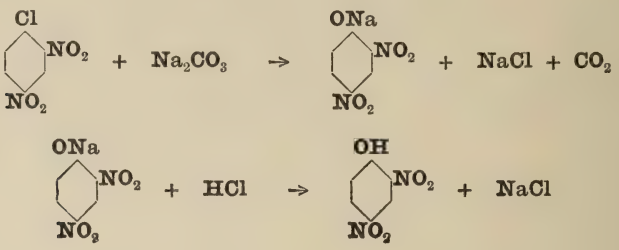
100 grams chlorodinitrobenzene, $Cl : (NO_2)_2 = 1 : 2 : 4$.
125 „ sodium carbonate (anhydrous).

The sodium carbonate is dissolved in 1120 c.c. water contained in a round flask, the chlorodinitrobenzene added, and the whole boiled for twenty-four hours, the flask being fitted with a reflux condenser.

After this time the whole of the oil will have gone into solution. The solution is acidified with hydrochloric acid, when the dinitrophenol separates out; this is filtered at the pump and dried in the air. Yield 91 grams.

Properties.—*m*-Dinitrophenol crystallises from water in pale yellow tables; M.P. 114°. On reduction it yields diamidophenol, which is used as a photographic developer (amidol). Dinitrophenol is used largely in the preparation of "Sulphur blacks."

Equation.—



CHAPTER XXVIII.

PREPARATIONS OF INTERMEDIATE PRODUCTS.

II. NAPHTHALENE SERIES.

18. *Naphthalene-β-sulphonic acid.*

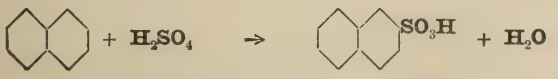
100 grams naphthalene.
120 ,, conc. sulphuric acid (67 c.c.).

The acid is warmed to 100° in a round flask, and the finely-ground naphthalene added gradually, the flask being well shaken. The mixture is now heated (without condenser) in an oil-bath to 160–170° for twelve hours. After cooling, the sulphonation mixture is poured into 1½ litres of water, heated to boiling, and milk of lime added until an alkaline reaction is obtained. (The amount of quicklime is calculated from the sulphuric acid, and is slaked with hot water.) The mixture is at once filtered through cloth, the filter-cloth is squeezed out into another dish, the liquid, if turbid, being filtered and added to the main quantity. The precipitated calcium sulphate is boiled up with 1 litre of water, filtered, and pressed. The united filtrates are evaporated down to a small bulk and allowed to cool. After standing overnight the calcium salt of the sulphonic acid crystallises out and is filtered at the pump. It is now dissolved in hot water, and a solution of sodium carbonate added till a filtered portion (10 c.c.) gives no further precipitate with sodium carbonate. (The weight of anhydrous sodium carbonate to be dissolved is calculated, assuming a theoretical yield of naphthalene sulphonic acid.) The precipitated calcium carbonate is now filtered at the pump, and the sodium salt evaporated till crystals begin to separate out.

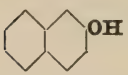
After standing overnight the crystals are filtered off and the filtrate further evaporated, when, after cooling and standing, a second crop may be obtained, which is added to the first, and the whole dried on the water-bath. Yield 120–140 grams.

Properties.—The acid forms non-deliquescent plates.

Equation.—



19. *β-Naphthol.*



100 grams sodium naphthalene-β-sulphonate.
300 „ powdered caustic soda.

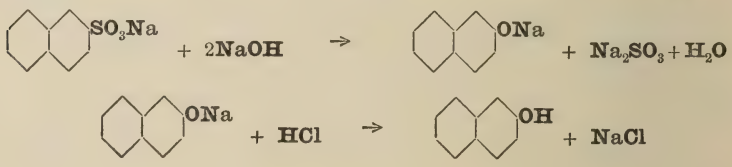
The caustic soda, together with 30 c.c. of water, is placed in a large copper or nickel crucible and the mixture heated to 280°. The thermometer is enclosed in a copper or nickel tube closed at one end and containing a little oil. A large cork is fitted to the open end of the tube, whereby the latter may be conveniently held and used as a stirrer. In this, as in all melting operations with caustic alkali, the eyes must be protected by glasses and the hands by thick gloves. The finely powdered β-salt is now added as quickly as possible, with constant stirring, but care must be taken that the temperature does not fall below 260°. When all is in, the temperature is raised to 320°, and the reaction takes place at 310–320°. The mass froths and steam is evolved, and when the mass becomes quite liquid the reaction is complete. The length of time for which the fusion is kept at 310–320° is about five minutes. The top layer of the melt, which is darker than the lower one and contains the sodium naphtholate, is now poured on to a copper plate with upturned edges, and, after cooling, the mass is broken up and dissolved in water. The naphthol is precipitated with concentrated hydrochloric acid (in the draught chamber). On the large scale the precipitation is sometimes brought about with a stream of carbon dioxide. After cooling, the β-naphthol is filtered off, dried, and distilled *in vacuo* (see p. 215). Yield 50–55 grams.

Properties.—Colourless, crystalline solid; M.P. 123°, B.P. 286°, sp. gr. 1·217; difficultly soluble in water (in 1000 parts cold and 75 parts boiling); easily soluble in organic solvents.

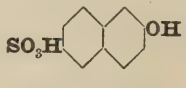
Use. - β-Naphthol is used largely in the preparation of azo- and other dyes; also in the production of "para-reds," etc., on the fibre.

For analysis, see page 314.

Equations.—



20. *β-Naphthol-6-sulphonic acid* (Schäffer's salt).



E.P. 7098[84].

100 grams β-naphthol.
200 „ conc. sulphuric acid (111 c.c.).

The β-naphthol is finely ground and gradually added to the sulphuric acid, which has been previously warmed to 30–40° in a round flask of about 400-c.c. capacity. The mixture is now heated on the water-bath to 100° for eight hours. The product is dissolved in about a litre of water and saturated with common salt. The sodium salt of the naphthol sulphonic acid separates out, and, after standing overnight, is filtered, washed well with saturated salt solution till free from acid, and dried. The sodium salt of the isomeric acid ("Bayer's acid," $OH : SO_3H = 2 : 8$), which is simultaneously formed, remains in the filtrate. Yield 100 grams.

Properties.—The sodium salt crystallises with two molecules of water. It is tested by titration with solution of potassium bromate.

Use.—Schäffer's salt is used largely for the preparation of azo-dyes; also for the preparation of "eikonogen" ($C_{10}H_5.(OH)(SO_3H).(NO) = 2 : 6 : 1$), used as a photographic developer.

Equation.—

21. *β-Naphthol-3 : 6-disulphonic acid* ("R salt")

E.P. 7097[84]; D.P. 33,916[84].

100 grams β-naphthol.
400 „ conc. sulphuric acid (222 c.c.).

The sulphuric acid is placed in a round flask of one-litre capacity and warmed on a sand-bath to 125°. The naphthol, finely powdered, is added fairly quickly, and the mixture kept at 125–126° for five to six hours. It is now poured into water and neutralised with milk of lime. The calcium sulphate is filtered off, boiled up again with hot water, and again filtered, both filtrates being united. A solution of sodium carbonate is now added till no further precipitate is obtained, and the calcium carbonate filtered off. The filtrate is saturated with salt, and the R salt separates out as a yellowish flocculent precipitate, which is filtered, washed with concentrated salt solution, and dried. Yield about 200 grams, 100 per cent.

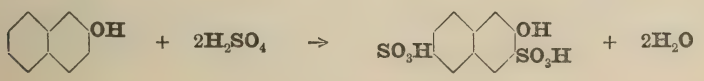
The product should be 80 per cent. (mol. wt. 348).

Properties.—The disodium salt is easily soluble in water, nearly insoluble in alcohol, and combines very easily with diazo-solutions.

R salt is tested with a standard solution of potassium bromate.

Use.—It is mostly used for the preparation of azo-dyes for wool.

Equation.—



22. α-*Nitronaphthalene*, $C_{10}H_7NO_2$.

Witt, *Chem. Ind.*, 1887, x. 216.

100 grams naphthalene.
80 „ conc. nitric acid, sp. gr. 1·4 (57 c.c.).
100 „ conc. sulphuric acid (56 c.c.).

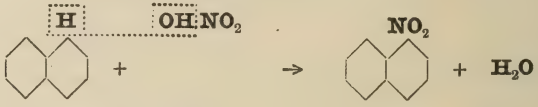
The acids are mixed as in the preparation of nitrobenzene, and transferred to a round flask of about 500-c.c. capacity. The naphthalene, which must have been finely ground in a mill (a coffee-mill answers the purpose), is added in small quantities at a time, the flask being well shaken and cooled after each addition. The temperature is kept at 45–50°. After all the naphthalene has been added, the mixture is warmed to 55–60° and poured into cold water. The nitronaphthalene sinks to the bottom and the acid is poured off. The solid cake is boiled up with water and the water poured away. The oil is now transferred to a large flask and subjected to steam distillation, whereby a little unattacked naphthalene is driven over and collects in the distillate. The contents of the flask are now poured into a large quantity of cold water, which is constantly stirred. The granulated nitronaphthalene is filtered off and dried in the air. Yield 130 grams.

Properties.—Light yellow solid, crystallising from alcohol in long needles; M.P. 61°, B.P. 304°, sp. gr. at 4°, 1·331.

α-Nitronaphthalene must have the correct melting-point and should not contain naphthalene (shown by distillation with steam).

Use.—It is used almost entirely for the manufacture of α-naphthylamine.

Equation.—



23. α-*Naphthylamine*.

Witt, *Chem. Ind.*, 1887, 215.
Paul, *Zeit. ang. Chem.*, 1897, 145.

60 grams α-nitronaphthalene.
80 „ iron powder.
4 „ conc. hydrochloric acid.

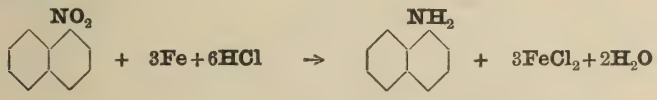
The iron powder, together with 40 c.c. water and the acid, is placed in a round flask and the mixture warmed to about 50°. The nitronaphthalene is now added in small portions at a time, and the flask well shaken after each addition. The temperature throughout the reduction must be kept at 70–80°. When the last

portion of nitronaphthalene has been added the flask is repeatedly shaken, and when no further rise of temperature is observed the reaction is finished. A little milk of lime is now added, till an alkaline reaction is obtained, and the mass allowed to cool. It is now filtered at the pump, and the iron residue containing the naphthylamine is dried as far as possible in the air. The residue is transferred to a small retort, the neck of which is connected by a rubber stopper with a thick glass filter-flask, the exit tube of the latter being connected with the vacuum pump. When the apparatus is exhausted the contents of the retort are carefully distilled over a free flame. A little water passes over at first and then the naphthylamine distils. The last portions are coloured red. The crude naphthylamine soon solidifies, and the cake is dried between filter-paper. It is purified by redistillation in vacuum from a clean retort. Care should be taken to avoid handling α-naphthylamine, as it imparts a most disagreeable smell to the fingers. If the distillation has been carefully carried out, a yield of 25–30 grams should be obtained.

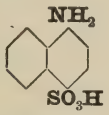
Properties.—α-Naphthylamine is nearly insoluble in water, and possesses a very disagreeable smell; B.P. 300°, M.P. 50°. The technical product forms greyish-white lumps. It should have nearly the correct melting-point, and dissolve almost completely in dilute hydrochloric acid.

Use.—α-naphthylamine is used for the preparation of α-naphthol, naphthylamine sulphonic acids, and many azo-dyes.

Equation.—



24. *Naphthionic acid.*



Nevile and Winther, *Ber.*, 1880, xiii. 1948; *J.C.S.*, xxxvii. 632.
E.P. 2237[83].
Witt, *Ber.*, 1886, xix. 578.
Paul, *Zeit. für ang. Chem.*, 1896, 685.

100 grams α-naphthylamine.
500 „ conc. sulphuric acid (278 c.c.).

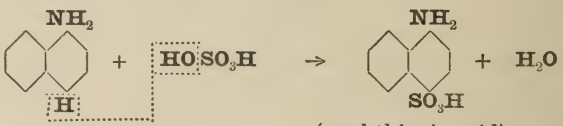
The naphthylamine is added to the acid contained in a round flask and heated to 100–120° for three to four hours, till a sample made alkaline and extracted with ether yields no naphthylamine on evaporation of the ether. The mixture is poured into water, when the difficultly soluble naphthionic acid separates out; this is filtered, washed with cold water till free from acid, and exactly neutralised by addition of caustic soda. The solution of the sodium salt is saturated with common salt and allowed to stand, when the sodium naphthionate separates out in white crystals. These are filtered at the pump, dried on a porous plate, then carefully in the steam oven. The dried substance may be extracted with alcohol or benzene, in order to remove a trace of α-naphthylamine. Yield about 140 grams of 100 per cent.

Properties.—The acid forms colourless needles, almost insoluble in cold water. The sodium salt is easily soluble in water, and crystallises with four molecules of water.

The technical product is the sodium salt. It should give a clear fluorescent solution with water. For analysis, a portion is extracted with alcohol and the filtrate evaporated to dryness; the residue, if any, is α-naphthylamine. The sodium naphthionate after extraction is tested with half-normal nitrite at the ordinary temperature. It should be about 70 per cent.

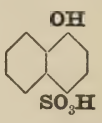
Use.—Sodium naphthionate is used largely in the manufacture of azo-colours.

Equation.—



(naphthionic acid).

25. *α-Naphthol sulphonic acid (1 : 4)* (Nevile and Winther's acid).



E.P. 16,807[99].

100 grams sodium naphthionate.
800 ,, sodium bisulphite solution, sp. gr. 1·37.

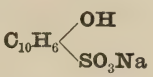
The naphthionate and sodium bisulphite are mixed in a round-bottomed flask fitted with a reflux condenser, 200 c.c. of water added, and the mixture boiled until no naphthionic acid can be detected (white precipitate with hydrochloric acid). This operation requires some hours. Caustic soda solution is now added until an alkaline reaction is obtained (Brilliant yellow paper), and the mixture boiled. Ammonia is evolved, and care must be taken that an alkaline reaction is maintained throughout this decomposition. When no more ammonia is evolved (a test should be made by withdrawing some of the liquid and boiling with more caustic soda), the liquid is poured into a slight excess of hydrochloric acid and boiled to expel all the sulphur dioxide. On cooling, or after evaporation if necessary, the naphthol sulphonic acid crystallises out and is filtered off by means of the pump and dried on a porous plate.

Two other methods of preparing this important acid may also be described. The first consists in heating a mixture of 100 grams of sodium naphthionate, 100 grams of sodium hydroxide, and 100 c.c. of water in an autoclave for eight to ten hours to 240–260°. After cooling, the product is dissolved in 750 c.c. of hot water and neutralised with hydrochloric acid. The solution is now saturated with salt, when the sodium salt of the naphthol sulphonic acid separates out in white crystals and is filtered and dried (D.P. 46,307[88]).

Secondly, the yellow, insoluble diazo-compound prepared from naphthionic acid is added gradually to boiling dilute sulphuric acid, and when nitrogen is no longer evolved the red solution is neutralised with sodium carbonate and used direct.

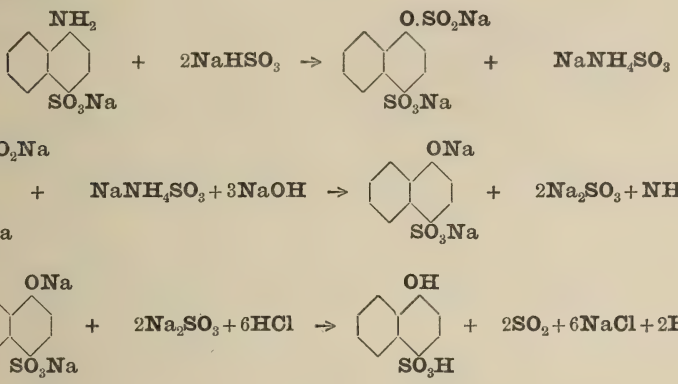
Analysis.—By titration with diazobenzene solution (p. 314).

Properties.—Both the free acid and its salts are very soluble in water. The sodium salt

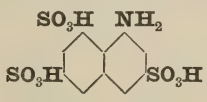


is largely used for the preparation of azo-dyes.

Equations.—



26. *α-Naphthylamine trisulphonic acid.*



E.P. 15,716[85]; D.P. 38,281[85]. E.P. 9258[90]; D.P. 56,058[90].

I. Preparation of naphthalene trisulphonic acid.—

100 grams sodium naphthalene-β-sulphonate.
187 „ fuming sulphuric acid, 40 per cent. SO_3.

The "β salt" is slowly mixed with the fuming acid in a round flask, keeping the temperature during the addition below 60°. The mixture is slowly warmed in an oil-bath to 125°, kept at this temperature for one hour, then raised to 160–170°, and heated at this temperature for ten hours.

II. Nitration of naphthalene trisulphonic acid.—

42 grams conc. nitric acid, sp. gr. 1·4 (30 c.c.).
60 „ conc. sulphuric acid (33 c.c.).

The sulphonation mixture is allowed to cool, and the mixture of nitrating acid added slowly. The mixture is cooled and frequently shaken, and the nitration carried on at 25–30°. When the whole of the acid has been added, the mixture is allowed to stand for a few hours.

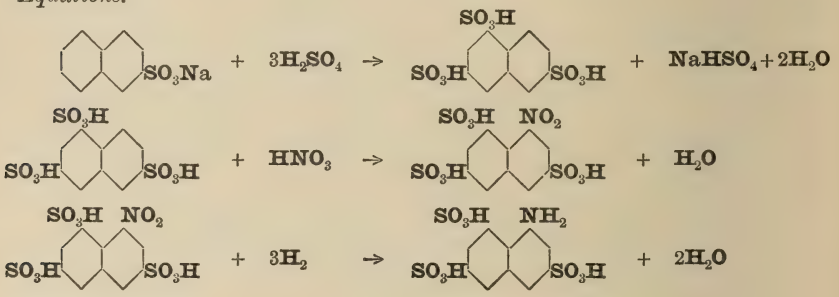
III. Reduction of the nitration mixture.—The nitration mixture is poured into water, the solution warmed to 40°, and powdered iron added gradually till the yellow colour of the nitro-acid vanishes (seen by placing a drop on filter-paper). Milk of lime is now added until an alkaline reaction is obtained, and the hot mixture filtered at the pump. The residue is boiled up with water and filtered again. The filtrate is treated with sodium carbonate solution till no further precipitate is obtained, and the calcium carbonate filtered off. The filtrate is evaporated down to a small bulk and acidified with hydrochloric acid, when the disodium salt of the naphthylamine trisulphonic acid crystallises out. After cooling, this is filtered and dried.

Properties.—The disodium salt is easily soluble in water, but difficultly soluble in salt solution or hydrochloric acid.

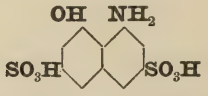
It is analysed by titration with half-normal nitrite solution.

Use.—The chief use of the acid is for the preparation of amidonaphthol disulphonic acid H and chromotropic acid (1 : 8 - dioxynaphthalene - 3 : 6 - disulphonic acid), which are used largely in the preparation of azo-dyes.

Equations.—


SO3Na + 3H2SO4 → SO3H SO3H SO3H + NaHSO4+2H2O
SO3H SO3H SO3H + HNO3 → SO3H NO2 SO3H SO3H + H2O
SO3H NO2 SO3H SO3H + 3H2 → SO3H NH2 SO3H SO3H + 2H2O

27. *Amidonaphthol disulphonic acid H.*



E.P. 13,443[90]; D.P. 69,722[90].

50 grams α-naphthylamine trisulphonic acid (disodium salt) 1 : 3 : 6 : 8.
100 „ powdered caustic soda.

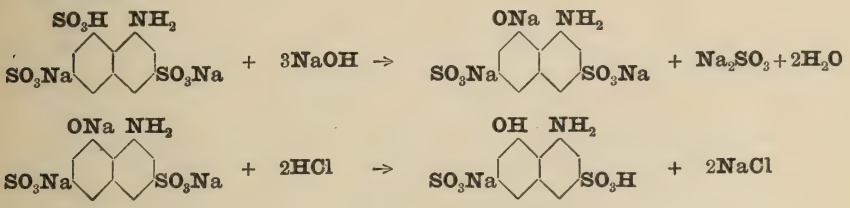
The caustic soda is dissolved with 10 c.c. of water in a nickel or copper crucible, the protected thermometer being used as a stirrer, as in the preparation of β-naphthol. The eyes and hands are also protected, as before. The soda is heated to 180°, and the finely powdered sodium salt added whilst stirring. The temperature is maintained at 180° till the melt has become clear and thin, when the reaction is finished. After cooling, the mass is dissolved in water and acidified with hydrochloric acid (in the draught chamber), when the acid sodium salt of H acid crystallises out. After standing overnight the acid is filtered at the pump and dried.

Properties.—The acid sodium salt forms white needles, and is difficultly soluble in cold water. Its aqueous solution shows a blue-red fluorescence.

It is analysed by titration with standard diazobenzene chloride solution in alkaline solution.

Use.—H acid is used for the preparation of violet to blue azo-dyes.

Equations.—



28. *β-Naphthylamine.*

Merz and Weith, *Ber.*, 1880, xiii. 1300; 1881, xiv. 2343.
Calm, *Ber.*, 1882, xv. 613.
Möhlau and Bucherer, *Farbenchemisches Praktikum*, 1908, p. 62.

100 grams β-naphthol.
150 c.c. ammonium sulphite solution (40 per cent. $(NH_4)_2SO_3$).
100 „ ammonia (20 per cent.).

The materials are well mixed together in an autoclave of about half a litre capacity. The autoclave is closed and heated at about 150° for about six hours. The temperature should not be allowed to rise much higher than this, otherwise some ββ-dinaphthylamine

will be formed.

When the reaction is finished (shown by the disappearance of the naphthol, which is soluble in caustic soda solution) the autoclave is allowed to cool completely, and the contents are filtered. The residue is treated with hot dilute caustic soda solution in order to free it from any unchanged β-naphthol, and then dissolved in dilute hydrochloric acid and the solution filtered from any ββ-dinaphthylamine that may be present. From the filtrate the base is precipitated by adding caustic soda solution, or the sparingly soluble β-naphthylamine sulphate is thrown down by the addition of a solution of sodium sulphate.

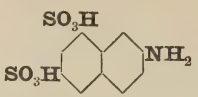
The base should be further purified by distillation in a vacuum.

Properties.—Plates, usually slightly coloured; M.P. 111–113°, B.P. 294°; slightly soluble in boiling water; gives no colour with ferric chloride.

β-Naphthylamine should be completely soluble in dilute hydrochloric acid, and have the right melting-point. It is used in the manufacture of red azo-dyes.

Equation.—

29. *β-Naphthylamine disulphonic acid G.*



E.P. 816[84]; D.P. 35,019[84].

100 grams β-naphthylamine.
390 „ fuming sulphuric acid, 25 per cent. SO_3.

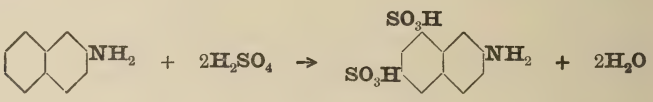
The β-naphthylamine is dissolved in sufficient hot water containing 70 grams concentrated hydrochloric acid (60 c.c.). A solution of 113 grams of crystallised sodium sulphate is added, whereby the sulphate of the base is precipitated $[(C_{10}H_7.NH_2)_2H_2SO_4]$. After cooling, this is filtered and dried.

The sulphate is finely ground and added to the fuming acid in a round flask, and the mixture is heated to 110–140° until a few drops dissolve clearly in water (about seven to eight hours). The sulphonation mixture is now poured into water, neutralised with milk of lime (alkaline reaction), the calcium sulphate filtered off, and the residue boiled up with water and again filtered. The solution containing the calcium salt is treated with sodium carbonate solution until no further precipitate occurs, and filtered. The solution is evaporated somewhat, acidified with hydrochloric acid, and potassium chloride added until no more dissolves. On cooling, the precipitated acid potassium salt is filtered and dried.

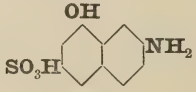
Properties.—The free acid and most of its salts are easily soluble in water It is analysed with standard solution of sodium nitrite.

"Amido-G salt" is used in the preparation of black azo-dyes for wool.

Equation.—



30. *Amidonaphthol sulphonic acid γ.*



E.P. 15,176[89], 16,699[89].

50 grams β-naphthylamine disulphonic acid G.
42 „ powdered caustic soda.

The caustic soda is dissolved in 50 c.c. of water and placed in an autoclave. The amido-G salt is well stirred in, the lid screwed on, and the vessel heated for six hours to 190–195°.

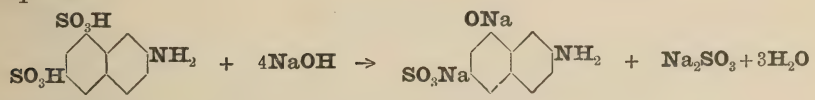
When the autoclave is quite cold it is opened, and the contents dissolved in water and acidified with hydrochloric acid in the draught chamber. On cooling, the γ acid crystallises out and is filtered and dried.

Properties.—The acid is difficultly soluble in water. The alkali salts dissolve easily with blue fluorescence.

The acid is tested by titration with standard solution of diazobenzene chloride in alkaline solution (sodium carbonate).

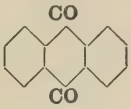
It is used very largely in the manufacture of azo-dyes, especially Cotton blacks.

Equation.—



(On acidifying, the free acid is obtained.)

31. *Anthraquinone.*



Cohen, *Practical Organic Chemistry.*

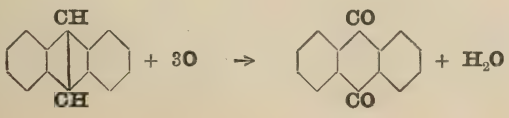
10 grams anthracene (pure).
120 c.c. glacial acetic acid.
20 grams chromium trioxide dissolved in 15 c.c. water and then 75 c.c. glacial acetic acid added.

The method used technically for the oxidation of anthracene, viz. with sodium bichromate and sulphuric acid in aqueous suspension, cannot be conveniently imitated in the laboratory, as, in order to obtain the anthracene in a sufficiently finely divided condition, it is sublimed in a current of superheated steam and condensed by fine jets of water. The finely powdered pure anthracene on the market is unattacked by this oxidising agent unless it undergoes the above process; for this reason the following method is more conveniently employed:—

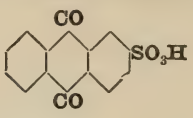
The anthracene is dissolved in the acetic acid by boiling them together in a round flask (half-litre) with upright condenser over wire gauze. The solution of chromium trioxide is then dropped in from a tap-funnel, pushed into the top end of the condenser, whilst the liquid is kept boiling. The operation should last about an hour. The solution becomes a deep green. It is allowed to cool, and is poured into water (500 c.c.), which precipitates the anthraquinone in the form of a brown powder. After standing an hour, it is filtered through a large folded filter, washed with a little hot water, then with warm dilute caustic soda and water again. Yield 10–12 grams. A portion of the dry substance may be purified by sublimation. It is placed (2–3 grams) on a large watch-glass, which is heated on the sand-bath over a very small flame. The watch-glass is covered with a sheet of filter-paper, which is kept flat by a funnel placed above. After five minutes or so pale yellow, needle-shaped crystals of anthraquinone will have sublimed on to the filter-paper.

Properties.—Yellow needles; M.P. 277°; sublimes at 250°; B.P. 382°; insoluble in water, soluble in acetic acid, less soluble in benzene and other organic solvents.

Equation.—



32. *Anthraquinone sulphonic acid.*



100 grams anthraquinone.
100 „ fuming sulphuric acid, 45–50 per cent. SO_3.

The acid is melted, if necessary, and the finely powdered anthraquinone added.

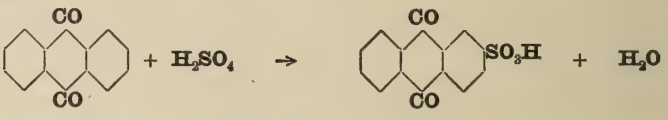
The mixture, which is contained in a round flask, is gradually heated in an oil-bath, so that at the end of one hour the temperature has reached 160°. The mixture is now slowly and carefully poured into hot water, the solution boiled for some time, and the unchanged anthraquinone filtered off at the pump. This amounts to 20–25 grams. The filtrate is neutralised with caustic soda and allowed to cool, when the greater part of the sodium anthraquinone sulphonate crystallises out. (This is the so-called "silver salt.") A second crop of crystals may be obtained by further concentration of the filtrate.

The final filtrate contains the sodium salt of anthraquinone disulphonic acid, which may be obtained, mixed with sodium sulphate, by evaporating to dryness.

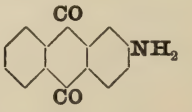
Properties.—The sodium salt crystallises from water with one molecule of water of crystallisation, having the formula $C_{14}H_7(SO_3Na)O_2 + H_2O$.

On melting with caustic alkali it is converted into alizarine.

Equation.—



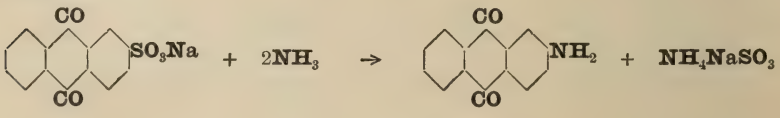
33. 2-*Amidoanthraquinone.*



One part of sodium anthraquinone sulphonate, as prepared in the preceding example, is mixed in an autoclave with 10 parts of concentrated aqueous ammonia (the weights taken depend on the size of autoclave; the latter should be filled to the extent of half its capacity), the lid of the autoclave screwed on carefully (see p. 210), and the vessel heated until the thermometer records 180°, and then maintained at this temperature for six hours. When the autoclave is quite cold the lid is removed and the amidoanthraquinone is filtered off, washed with hot water, and dried.

Properties.—2-Amidoanthraquinone forms dark-red needles melting at 302°. It is readily soluble in hot hydrochloric acid, and fairly easily in alcohol or benzene. When melted with caustic alkali it yields indanthrene.

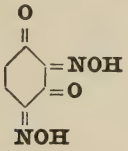
Equation.—



CHAPTER XXIX.

PREPARATION OF DYESTUFFS.

1. *Fast green O* (dinitrosoresorcin).



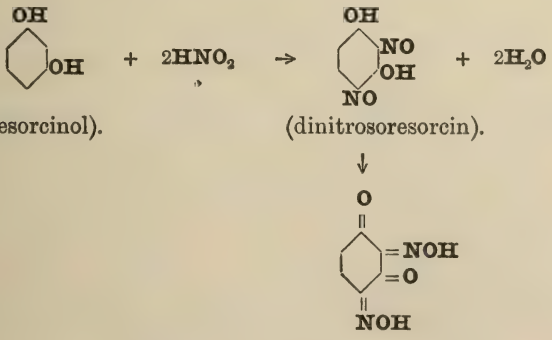
Goldschmidt and Strauss, *Ber.*, 1887, xx. 1607.
Kostanecki, *Ber.*, 1887, xx. 3147.
J.S.C.I., 1890, 1126.

20 grams resorcinol.
45 „ conc. hydrochloric acid (39 c.c.).
25·5 „ sodium nitrite.

The resorcinol is dissolved in 800 c.c. of water and the hydrochloric acid added, together with 100 grams of common salt. Ice is added till the temperature is 0°, and into this solution, which is stirred mechanically, the sodium nitrite, dissolved in 100 c.c. of water, is allowed to flow very slowly, the temperature not being allowed to rise above 8°. This takes about half an hour. When all the nitrite has been added, the liquid should show a faintly acid reaction. After standing for one hour, the brownish-yellow precipitate is filtered, washed with ice-cold water, and the paste dried on a porous plate. Yield 36 grams.

Properties. — Greyish-brown powder, soluble in hot water. Dyes iron-mordanted cotton green ; iron-mordanted wool dark green.

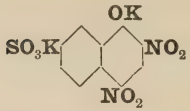
Equation.—



(resorcinol). (dinitrosoresorcin).

For the explanation of this formula, see page 44.

2. *Naphthol yellow S.*



E.P. 5305[79]; A.P. 225,108[80]; D.P. 10,785[79]; F.P. 134,632[80]; E.P. 11,318[87].

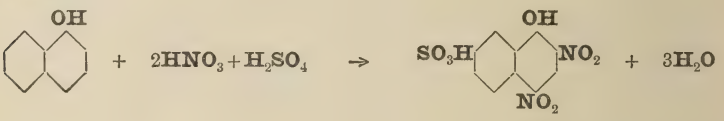
100 grams α-naphthol.
400 „ conc. sulphuric acid (222 c.c.).
174 „ conc. nitric acid.

The sulphuric acid is warmed to 100° in a round flask, and the naphthol, in small pieces, is added all at once. The temperature is now raised to 120°, and kept at this point for three to four hours. The sulphonation mixture is then poured into 600 c c. of water and stirred mechanically. As soon as the temperature is about 30°, the solution is poured into a mixture of 90 grams of nitric acid with 33 c.c. of water, the temperature being kept below 35°. A further 84 grams of nitric acid is now added, during which addition the temperature may rise to 40°. The nitration mixture is now filtered on woollen cloth and washed free from acid with salt solution. The drained paste is stirred with hot water at 80°, sodium carbonate added until neutral, and the dyestuff is precipitated by adding potassium chloride (about 75 grams). It is then filtered and dried on a porous plate.

Properties.—Orange yellow powder. Dyes wool and silk yellow from an acid bath.

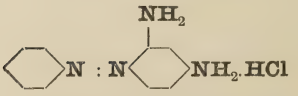
Analysis.—With Night blue (p. 342).

Equation.—



Naphthol yellow S (free acid).

3. *Chrysoïdine.*



Ber., 1877, x. 213, 350, 388, 654.

9·3 grams aniline.
30 c.c. conc. hydrochloric acid.
7·2 grams sodium nitrite.
11 „ meta-phenylenediamine (or an equivalent solution).

The aniline is mixed with about 100 c.c. of water in a heavy beaker and ice

added. The acid is poured in and the solution diazotised by adding slowly a solution of 7·2 grams of sodium nitrite, the whole being continually stirred. The nitrite solution is added in small portions at a time, and after each addition a drop is withdrawn from the solution and placed on iodide-starch paper; if a reaction is obtained the mixture is stirred further, and tests are frequently made till no blue coloration is seen on the paper. The next portion of nitrite solution may now be added. Towards the end the nitrite is added in very small portions, and the solution is continually tested so as to avoid any excess of this reagent. If the diazotisation has been properly carried out, no smell of nitrous gases should have been detected, and the test-paper should be only faintly coloured blue by the solution after the latter has stood for five minutes.

If too much nitrite is present, a few drops of aniline may be added. The temperature throughout the diazotisation must be kept below 5°, by adding more ice if necessary, and the solution of the diazo-salt must be perfectly clear.

In order to combine it with the phenylenediamine, the latter is dissolved in about 200 c.c. of cold water; if the diamine is already in solution, it must be rendered just acid with hydrochloric acid, if necessary, and diluted to 200 c.c. This is placed in a thick beaker or basin and agitated by a mechanical stirrer. The diazo-solution is then poured in and the mixture allowed to stir for some time. A few drops are now withdrawn by a pipette, put into a test-tube, and shaken with a few grams of salt till the colouring matter is precipitated. A little of this is dropped on filter-paper, when a colourless rim spreads from the drop of colour. A drop of diazo-solution is now placed on one side of this rim, so as to mix with it, and a brownish-yellow line should appear at the junction of the two liquids, showing the presence of an excess of *m*-phenylenediamine. In case this reaction is not obtained, another drop is tested in like manner with a solution of the diamine, and if a reaction is here obtained an excess of diazo-solution is present, and *m*-phenylenediamine solution must be added until a slight excess is present. If a reaction is obtained in both the above cases, the combination is not complete and the stirring must be continued.

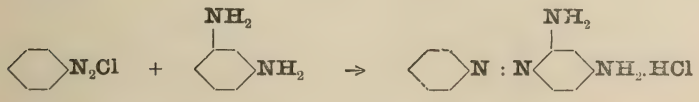
The solution is now heated to 60° and a concentrated solution of salt is added until a sample, on cooling, indicates that the colouring matter will crystallise out. When the whole is cold the chrysoïdine will have separated in small crystals, which are filtered off and dried.

Properties.—Reddish-brown crystals, soluble in water with a yellow colour. Dyes wool, silk, and tannin-mordanted cotton orange.

Equations.—

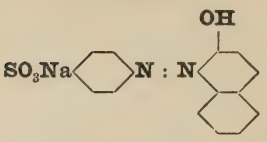
(1)

(aniline). (diazonium chloride).

(2) 

(*m*-phenylenediamine). (Chrysoïdine).

4. *Orange II.*



Mühlhäuser., *Dingl. pol. J.*, 1887, cclxiv. 187, 238;
J.S.C.I., 1887, 591.
Paul, *Z. für ang. Chem.*, 1896, 686.

17·3 grams sulphanilic acid.
7·2 „ sodium nitrite.
14·4 „ β-naphthol.

The sulphanilic acid is dissolved in water by careful addition of caustic soda solution (on the large scale, using the crude product, the solution is boiled for a few minutes in order to drive off traces of aniline and then filtered). Ice is added till the temperature is 5°, the volume of the whole being about 500 c.c. 30 c.c. of concentrated hydrochloric acid are poured in, and then the sodium nitrite, dissolved in a small quantity of water (or 100 c.c. of a normal solution), added slowly. Tests are made from time to time with starch-iodide paper, and a slightly blue coloration should be obtained when all the nitrite has been added. The diazo-compound separates out in fine white needles.

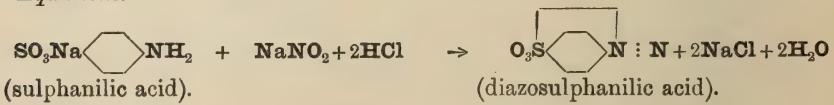
(*Note.*—This should never be filtered and allowed to dry, as it is extremely explosive.)

The β-naphthol is dissolved by heating it with a solution of 4·5 grams of caustic soda in 15 c.c. of water, and the sodium naphtholate solution thus formed is poured into 160 c.c. of cold water, and this cooled, if necessary, to about 15°. This solution is stirred by a mechanical stirrer, and the diazo-solution (or diazo-compound in suspension) run in gradually. When the whole of the diazo-solution has been added, the mass should show a weak alkaline reaction (test with brilliant-yellow paper), and practically no excess of either component (diazo-compound or β-naphthol) should be present. Although it is usual to leave a slight excess of the phenol or amine in the preparation of azo-dyes, yet in this case an excess of β-naphthol has a bad effect on the shade of the dye produced, and it is better to leave a slight excess of diazo-solution in the mixture. The mass is stirred for an hour longer, when nearly the whole of the colouring matter will have separated out. A little salt solution is added, so as to precipitate nearly the whole of the dye. A test on filter-paper should show a pale orange rim. It is now filtered at the pump, dried at 80°, and ground. Yield 34 grams.

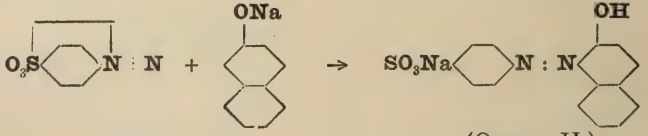
Properties.—Bright orange powder, soluble in water with orange colour. Dyes wool orange from an acid bath.

Analysis.—With standard solution of titanous chloride (see p. 336).

Equations.—

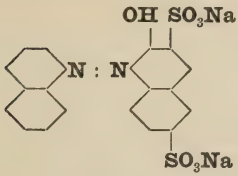


(sulphanilic acid). (diazosulphanilic acid).



(Orange II.).

5. *Fast red B* (Bordeaux B).



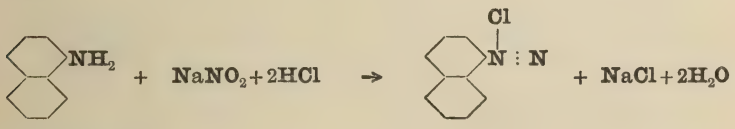
E.P. 1715[78]; A.P. 251,164; D.P. 3229[78]; F.P. 124,811.

14·3 grams α-naphthylamine
7·2 „ sodium nitrite.
35 „ "R salt"

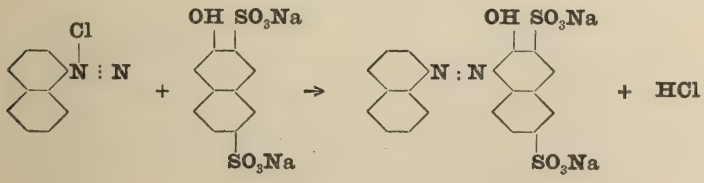
The naphthylamine is dissolved in 300 c.c. of hot water and 10 c.c. of concentrated hydrochloric acid. The clear solution is cooled by addition of ice, and then 20 c.c. of concentrated hydrochloric acid added; the temperature must be reduced to 0–4°. The sodium nitrite (dissolved in a little water) is now poured in fairly quickly, and a slightly brown coloured solution of the diazo-salt is obtained. This should be perfectly clear; if a brown precipitate of diazoamidonaphthalene appears, a fresh solution must be prepared, adding, if necessary, 25 c.c. of acid instead of 20 c.c. This diazo-solution is now added slowly to the "R salt" solution, which has been prepared by dissolving 35 grams of "R salt" (this quantity is calculated for the pure substance—mol. wt. 348; if a less pure "R salt" is used, a proportionally greater quantity must be taken) in 400 c.c. of water, adding 8·5 grams of caustic soda and cooling to 15°. During the addition the whole is well stirred mechanically, and an alkaline reaction and excess of "R salt" must be detected when the combination is finished. After stirring for one hour the colour is heated to 80°, salt added until the colouring matter is nearly all precipitated, when it is filtered, dried, and ground. Yield 50–55 grams.

Properties.—Brown powder, dissolving in water with magenta-red colour. Dyes wool red from an acid bath.

Equation.—

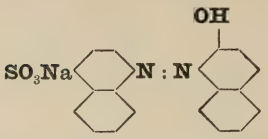


(α-naphthylamine)



(Fast red B).

6. *Fast red A* (Roccelline).



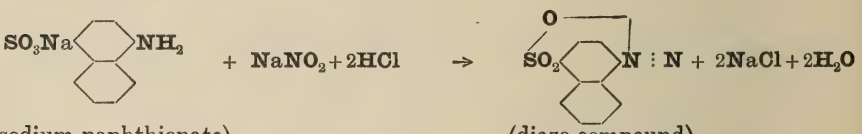
E.P. 786[78]; A.P. 204,799; D.P. 5411[78]; F.P. 123,148[78].

24·5 grams sodium naphthionate, 100 per cent.
7·2 „ sodium nitrite.
15 „ β-naphthol.

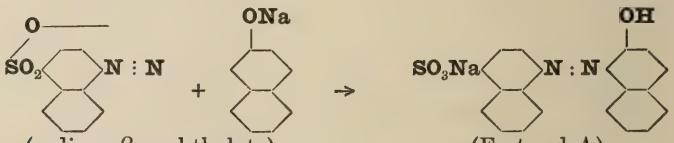
The above quantity of sodium naphthionate is calculated for the pure substance (mol. wt. = 245). If material of less strength than this is used, a proportionally larger amount must, of course, be taken. It is dissolved in water and diazotised as described for amido-G salt (p. 265). The diazo-compound is filtered and mixed with water to a thin cream. This is poured slowly into the β-naphthol solution, which is stirred by a mechanical stirrer, and prepared by heating the naphthol with a solution of 4·5 grams of caustic soda in 15 c.c. of water and pouring into 160 c.c. of cold water. The solution of sodium β-naphtholate should not be above 15°. When the whole of the diazo-compound has been added, a slight excess of β-naphthol should be detected (by salting out a few drops in a test-tube, pouring a drop on paper, and testing the rim with a diazo-solution), and an alkaline reaction should be obtained with brilliant-yellow paper. After an hour's stirring the colour is heated to 80°, salt added until nearly the whole of the colouring matter is precipitated, and then filtered, dried, and ground.

Properties.—Brownish-red powder, dissolving in hot water with brown-red colour. Dyes wool red from an acid bath.

Equations.—

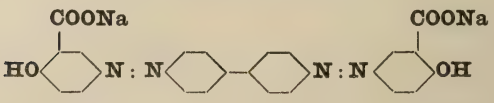


(sodium naphthionate). (diazo-compound).



(sodium β-naphtholate). (Fast red A).

7. *Chrysamine G.*



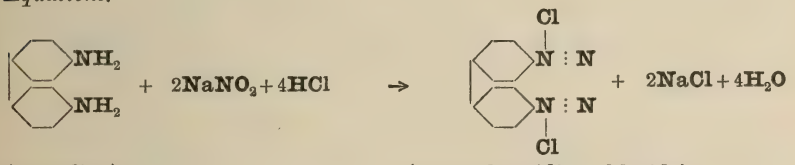
E.P. 9162[84]; A.P. 329,638; D.P. 31,658[84].

18·4 grams benzidine.
32 „ salicylic acid.

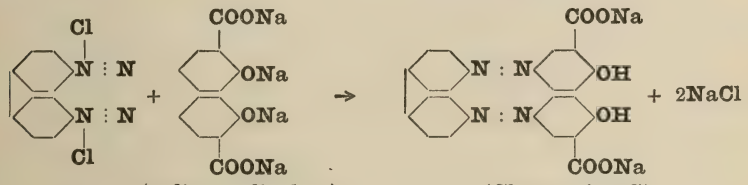
The benzidine is dissolved in 300 c.c. of hot water containing 20 c.c. of concentrated hydrochloric acid; the solution is cooled with ice to 5°, 30 c.c. of concentrated hydrochloric acid added, and the solution tetrazotised with 14·4 grams of sodium nitrite dissolved in a little water. The solution must be clear and give a faint blue colour with iodide-starch paper. The salicylic acid is dissolved in 200 c.c. of cold water with addition of 9·5 grams of caustic soda, and the tetrazo-solution poured into it whilst stirring mechanically. The whole is well stirred for a day, during which time a solution of 12 grams of caustic soda is very slowly added. At the end of this time no tetrazo-compound should be present (test with R salt); but if the combination is not quite complete, it must be stirred during the following day. The solution must also show an alkaline reaction. The colouring matter is entirely precipitated, so that no salt is added, and it is filtered cold, dried at 40–50°, and ground.

Properties.—Yellowish-brown powder, sparingly soluble in water with brownish-yellow colour. Dyes unmordanted cotton yellow from a soap-bath.

Equations.—

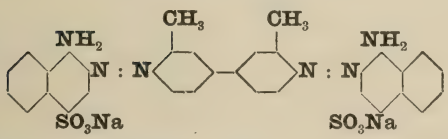
(1) 

(benzidine). (tetrazobenzidine chloride).

(2) 

(sodium salicylate) (2 mols.). (Chrysamine G).

8. *Benzopurpurine 4B.*



E.P. 3803[85]; A.P. 329,632; D.P. 35,615[85]; F.P. 167,876.

21·2 grams tolidine.
150 „ sodium naphthionate, 100 per cent.

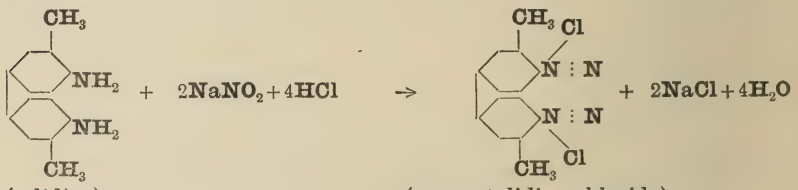
The tolidine is dissolved in 300 c.c. of hot water containing 20 c.c. of concentrated hydrochloric acid, cooled with ice to 5°, 30 c.c. of concentrated hydrochloric acid added, and the solution diazotised with a solution of 14·4 grams of sodium nitrite in a little water. The diazo-solution must be quite clear and give a slight reaction with iodide-starch paper. This is now poured into a

cold concentrated solution of 150 grams of sodium naphthionate (a large excess, whereby a better yield is obtained than when the theoretical amount is used), and the mixture stirred mechanically for two (or more) days. After the first half-hour's stirring a solution of 35 grams of sodium carbonate (Na_2CO_3) is added, a few drops at a time, so that the whole has been used by the end of the second day. On the next day the colouring matter is heated to 80° and a little salt added, so that the solution remains slightly yellow in colour. The precipitated colour is filtered, dried, and ground. (If the filtrate is acidified the precipitated naphthionic acid can be filtered off and used over again by dissolving it in sodium carbonate.)

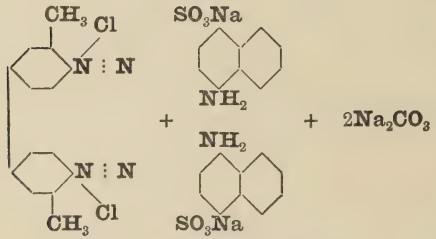
Properties.—Brown powder, dissolving in water with brownish-red colour. Dyes cotton direct from an alkaline bath, red.

Analysis with standard solution of titanous chloride (see p. 338).

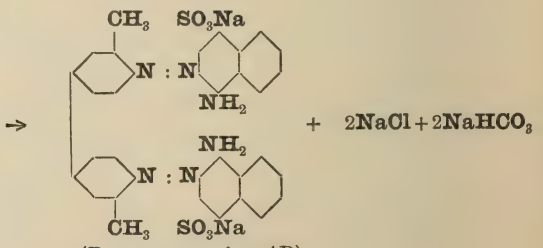
Equations.—

(1) 

(tolidine). (tetrazotolidine chloride).

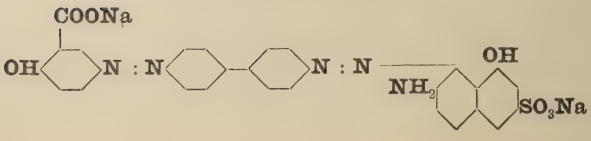
(2) 

(sodium naphthionate) (2 mols.).



(Benzopurpurine 4B).

9. *Diamine fast red.*



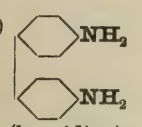
E.P. 16,699[89]; D.P. 55,648[89].

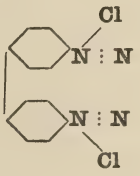
18·4 grams benzidine.
14·4 „ salicylic acid.
25 „ γ acid.

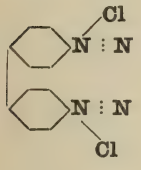
The benzidine is tetrazotised as described on p. 259, and the clear solution added to a cold solution of 14·4 grams of salicylic acid in 45 grams of sodium carbonate (Na_2CO_3) and 500 c.c. of water. This mixture is stirred for two to four hours, when the formation of the intermediate product is complete, and no free tetrazo-solution can be detected in solution. The mixture is now acidified carefully with hydrochloric acid, so that a slightly acid reaction is obtained; a solution of 14 grams of sodium acetate ($C_2H_3O_2Na.3H_2O$) added, and finally a neutral solution of 25 grams of γ acid in 11 grams of sodium carbonate (if this is alkaline, it must be neutralised with a few drops of acetic acid). The mixture is well stirred for several hours, when the combination should be complete. A little more sodium acetate may be added in case it is not, and the whole stirred longer. The colouring matter is now made alkaline with sodium carbonate solution, heated to 80°, and salt added till only a faint yellowish colour remains in solution. It is filtered, dried, and ground.

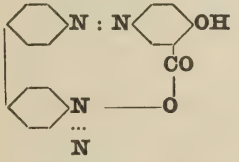
Properties.—Brownish-red powder, dissolving in water with red colour. Dyes unmordanted cotton and chromed wool a fast red.

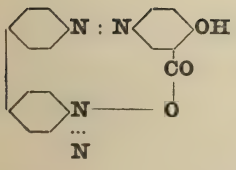
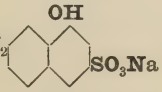
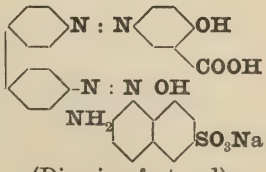
Equations.—

(1) 
(benzidine).

$+ 2NaNO_2 + 4HCl \rightarrow$ 
$+ 2NaCl + 4H_2O$

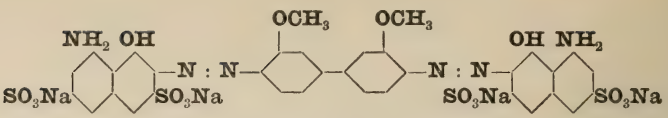
(2) 
$+$
(sodium salicylate).
$+ Na_2CO_3$

$\rightarrow$ 
(intermediate product).
$+ 2NaCl + NaHCO_3$

(3) 
$+ NH_2$ 
(γ acid).
$\rightarrow$ 
(Diamine fast red).

On adding sodium carbonate to this, the COOH group becomes COONa.

10. *Benzo sky blue.*



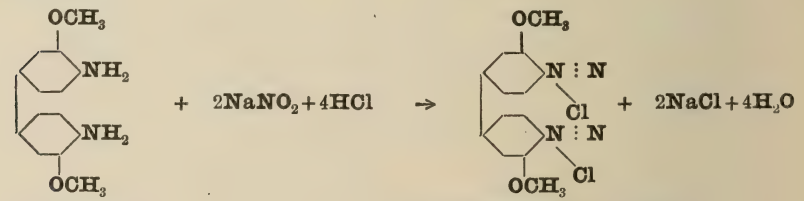
E.P. 1742[91]; A.P. 464,135; D.P. 74,593; F.P. 201,770.

12·2 grams dianisidine.
35 „ "H acid" (acid sodium salt, mol. wt. 341).

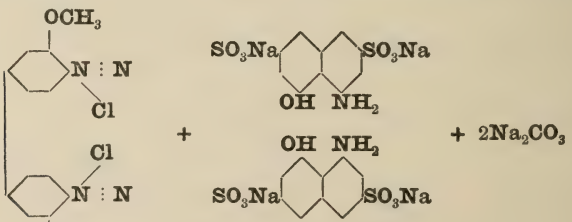
The dianisidine is dissolved in 10 c.c. of concentrated hydrochloric acid and about 200 c.c. of boiling water. The solution is cooled to 5° with ice, 20 c.c. of concentrated hydrochloric acid added, and then a solution of 7·2 grams of sodium nitrite slowly poured in till a blue reaction is obtained with iodide-starch paper. The clear tetrazo-solution is added slowly to a cold solution of 35 grams of H acid in 35 grams of sodium carbonate (Na_2CO_3) and 400 c.c. of water. When all is added, an alkaline reaction must be shown by the mixture and excess of H acid must be present. After stirring for an hour the colour is heated to 80°, salt added till only a reddish-blue colour remains in solution, and the solution is filtered, dried, and ground.

Properties.—Bluish-grey powder, dissolving in water with a blue colour. Dyes cotton direct from an alkaline bath.

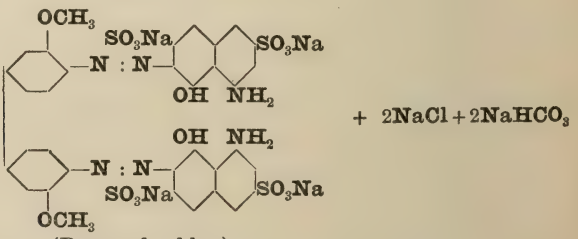
Equations.—



(dianisidine). (tetrazodianisidine chloride).

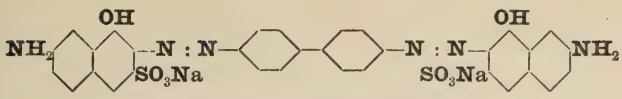


("H acid") (2 mols.).



(Benzo sky blue).

11. *Diamine black RO.*



E.P. 16,699[89]; D.P. 55,648[89].

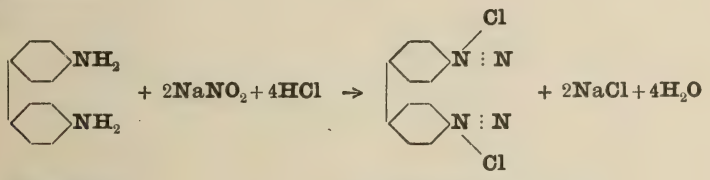
18·4 grams benzidine.
50 „ "γ acid" (amidonaphthol sulphonic acid γ, $NH_2 : OH : SO_3H = 2 : 8 : 6$; mol. wt. 239).

The benzidine is tetrazotised as in the preparation of Chrysamine G, and the solution is added slowly to a cold solution of 50 grams of γ acid in 60 grams of sodium carbonate and 500 c.c. of water. The γ acid solution must be very well stirred during the addition, so as to avoid any part of the solution becoming acid, as in this case some of the tetrazo-compound may combine in the ortho-position to the amido-group, forming a little Diamine violet, which would redden the shade of the finished colour. At the end an alkaline reaction must be obtained and an excess of γ acid must be present. After stirring for an hour the colouring matter is heated to 80°, salted till only a reddish-black colour remains in solution, filtered, dried and ground.

Properties.—Black powder giving a violet black solution. Dyes unmordanted cotton greyish violet; after diazotisation on the fibre and combination with β-naphthol or *m*-phenylenediamine, gives a deep blue or black fast to washing, light, alkalies, and acids.

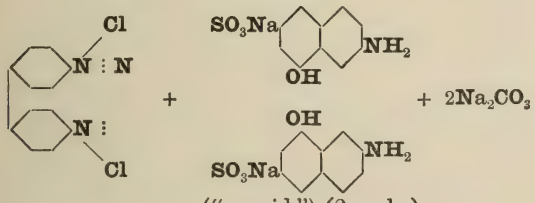
Equations.—

(1)

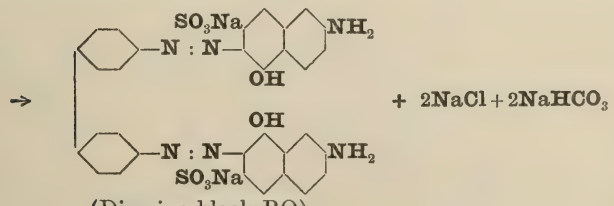


(benzidine). (tetrazobenzidine chloride).

(2)

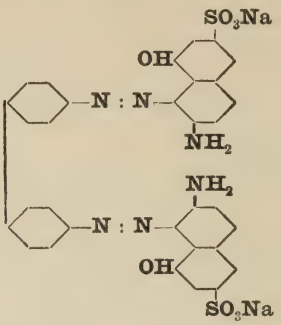


("γ acid") (2 mols.).



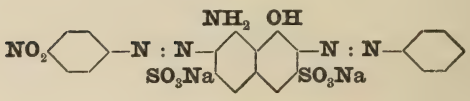
(Diamine black RO).

Diamine violet N [C] is formed by the combination of the above constituents in *acid* solution; its formula is



(Diamine violet N).

12. *Naphthol blue-black.*



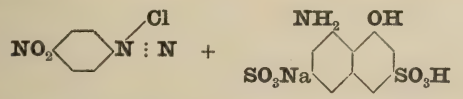
E.P. 6972[91]; A.P. 480,326; D.P. 65,651[91]; F.P., fourth addition to 201,770.

7	grams	*p*-nitraniline.
3·6	„	sodium nitrite.
17·05	„	"H acid" (acid sodium salt of 1 : 8-amido-naphthol-3 : 6-disulphonic acid).
4·65	„	aniline.
3·6	„	sodium nitrite.

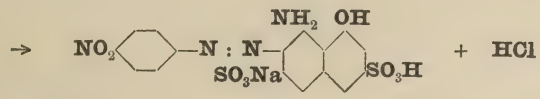
The *p*-nitraniline is dissolved by boiling with 20 c.c. concentrated hydrochloric acid and 20 c.c. of water. After cooling, the solution is poured into 200 c.c. of water and ice added till the temperature is 10°. The sodium nitrite (3·6 grams), dissolved in a little water, is now added *all at once*, and the whole well stirred. A reaction must be obtained with iodide-starch paper. If the diazotisation has been properly carried out, no precipitation of the diazoamido-compound should occur. The diazo-solution is now poured into a neutral solution of "H acid," made by dissolving 17·05 grams (mol. wt. = 341) in 200 c.c. of water with addition of sodium carbonate solution, and carefully neutralising any excess of alkali with hydrochloric acid. The temperature of this solution should be 15°, and during the combination the whole is stirred mechanically. After stirring for half an hour the bluish-red solution is carefully neutralised with aqueous sodium carbonate, and, when neutral, a solution of 15 grams of sodium carbonate is further added. To this blue solution is now added a solution of diazobenzene chloride prepared from 4·65 grams of aniline, 15 c.c. of concentrated hydrochloric acid, and 3·6 grams of sodium nitrite, as described on page 254, and the whole stirred for an hour longer. The mixture must show an alkaline reaction, and when finished is heated to 80° and salted until nearly the whole of the colouring matter is precipitated; this is filtered, dried, and ground.

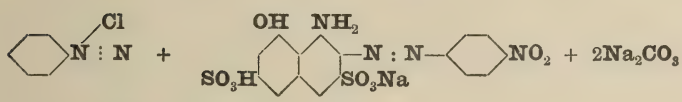
Properties.—Dark powder, dissolving in water and giving a dark blue solution. Dyes wool blue-black in an alkaline bath.

Equations.—

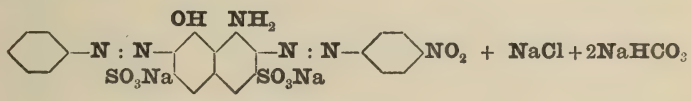


(diazo-*p*-nitraniline chloride). (H acid). (in acid solution).





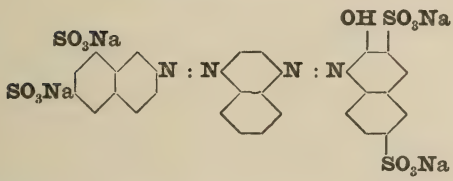
(diazobenzene chloride).



(Naphthol blue-black).

(In alkaline solution.)

13. *Naphthol black B.*



E.P. 9214[85]; A.P. 345,901; D.P. 39,029; F.P. 170,342.

17·05 grams "amido-G salt" (acid potassium salt, mol. wt. = 341).
7·2 „ α-naphthylamine.
15 „ "R salt."

The amido-G salt (β-naphthylamine-6 : 8-disulphonic acid) is dissolved in 250 c.c. of water, the solution cooled to 10°, and 15 c.c. of concentrated hydrochloric acid added. The amido-compound is converted into the corresponding diazo-salt by adding a solution of 3·6 grams of sodium nitrite, and care must be taken that no excess of the latter is present. If a reaction is obtained with iodide-starch paper, a few drops of a solution of amido-G salt are added till no blue coloration is given by the diazo-solution. This is stirred mechanically,

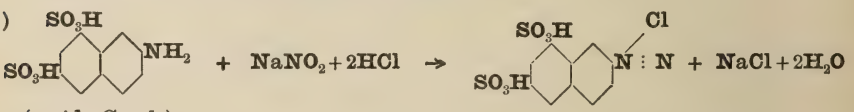
and a cold solution of 7·2 grams of α-naphthylamine in 5 c.c. of concentrated hydrochloric acid and 100 c.c. of water run in. The mixture is stirred for several hours, warmed to 50°, and caustic soda solution added until an alkaline reaction is obtained.

The latter is difficult to detect with the ordinary test-papers, and in this and other cases, where the colour or solubility of the substance to be tested prohibits the direct use of test-papers, the following method is adopted:—A crystal of ammonium chloride is added to a few drops of the solution placed on a watch-glass, and the latter gently warmed with a very small flame; a second watch-glass with a piece of moistened red litmus-paper adhering to its concave side is placed over the other one, and if the liquid is alkaline the litmus-paper will be turned blue. If this reaction is not obtained, more caustic soda must be added to the solution and the test repeated.

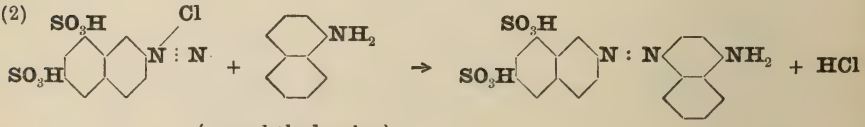
The alkaline solution is now heated to boiling, the flame removed, and salt added until no more can be dissolved. On cooling, most of the colouring matter is precipitated and is filtered. The paste is not dried, but immediately diazotised and further combined. It is dissolved in 400 c.c. of cold water, and diazotised by adding 25 c.c. of concentrated hydrochloric acid and a solution of 3·6 grams of sodium nitrite, the whole being cooled with ice to about 10°. (The solution is not tested with iodide-starch paper, as an excess of nitrite must be used. The mixture is stirred for several hours, and may, with advantage, be left standing overnight. The diazo-solution is now combined, whilst stirring, with a solution of 15 grams of "R salt" (mol. wt. = 348), dissolved in 180 c.c. of water, and 18 grams of sodium carbonate (Na_2CO_3). After an hour's further stirring the colouring matter is heated to 80°, and salt added till the blue-black dye is precipitated and a dark red colour remains in solution (shown by spotting on filter-paper). This is now filtered, dried, and ground.

Properties.—Black powder, soluble in water with violet colour. Dyes wool bluish-black from an acid bath.

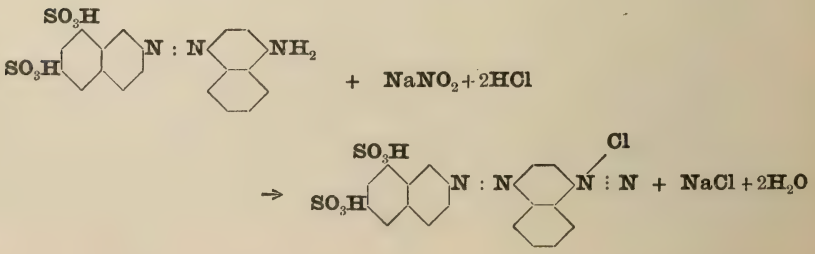
Equations.—Free acids only are written.

(1) 

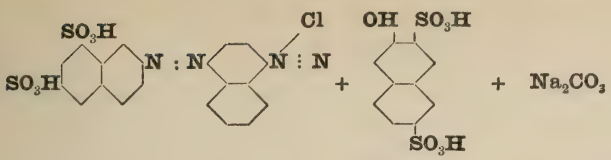
(amido-G salt).

(2) 

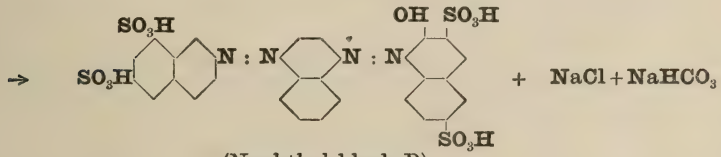
(α-naphthylamine).

(3) 

(4)



(R salt).

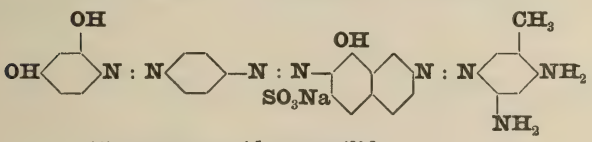


(Naphthol black B).

Note.—The formula of this dye is always written as the tetrasodium salt, but if the acid *potassium* salt of amido-G salt is used (this being stable in the presence of hydrochloric acid), the dye should be, apparently, the potassium trisodium salt. For the sake of simplicity, therefore, we have adopted the above method of expressing the reactions.

14. *Isodiphenyl black.*

E.P. 20,278[97]; A.P. 615,497; F.P. 270,151.



15 grams *p*-amidoacetanilide.
24 „ amidonaphthol sulphonic acid γ.
10 „ resorcinol.
10 „ *m*-toluylenediamine.

The amidoacetanilide is dissolved in water with the addition of 30 c.c. of concentrated hydrochloric acid, the solution cooled with ice to 0–5°, and diazotised by adding 7·2 grams of sodium nitrite dissolved in water. This diazo-solution is poured into 24 grams of γ acid dissolved in 25 grams of anhydrous sodium carbonate and 250 c.c. of water. The well-stirred mixture must be tested continually during the addition, in order that an excess of alkali may be present. If the addition of the diazo-solution causes foaming, more sodium carbonate must be added. After stirring for a few hours the azo-colouring matter is heated to 80° and saturated with salt. On cooling, it is filtered.

The reddish cake of colouring matter is transferred to a flask (or, better, an enamelled pan), mixed with a solution of 16 grams of caustic soda, and heated for about three hours until a nearly clear solution is obtained. The saponified product is allowed to cool, ice added till the temperature is 0°, and tetrazotised by the addition of 100 c.c. concentrated hydrochloric acid and 13–13·5 grams of sodium nitrite dissolved in water. The solution is continually tested with Congo paper during the diazotisation, and an excess of acid must be present. It is best to use a normal solution of sodium nitrite, and during its addition to test constantly with iodide-starch paper, so that the exact quantity necessary may be known. The above quantities of resorcinol and *m*-toluylenediamine are calculated for 13 grams of nitrite; if a greater or less quantity is used, the amounts of the

two components will, of course, vary in proportion. When this operation is finished a clear red solution is obtained.

This solution is now poured into a cold solution of 65 grams of sodium carbonate (Na_2CO_3), and then, immediately, the resorcinol, dissolved in a little water. The solution must show an alkaline reaction. After making this test the solution of *m*-toluylenediamine in water is added, and the colouring matter is complete (*m*-toluylenediamine is used here instead of *m*-phenylenediamine, which is actually employed on the large scale; the shade produced is practically the same).

After stirring for an hour longer the dye is filtered and dried.

Properties—Black powder, soluble in hot water with a violet-black colour. Dyes unmordanted cotton black.

Equations.—

(1) $(C_2H_3O)HN{\bigcirc}NH_2 + NaNO_2 + HCl \rightarrow (C_2H_3O)HN{\bigcirc}N{:}N\text{–Cl} + NaCl + 2H_2O$

(*p*-amidoacetanilide).

(2) $(C_2H_3O)HN{\bigcirc}N{:}N\text{–Cl} + HO{\bigcirc}(SO_3Na)NH_2 + Na_2CO_3$

("γ acid").

$\rightarrow (C_2H_3O)HN{\bigcirc}N{:}N\text{–}HO{\bigcirc}(SO_3Na)NH_2 + NaCl + NaHCO_3$

(3) $(C_2H_3O)HN{\bigcirc}N{:}N\text{–}HO{\bigcirc}(SO_3Na)NH_2 + NaOH$

$\rightarrow H_2N{\bigcirc}N{:}N\text{–}HO{\bigcirc}(SO_3Na)NH_2 + CH_3COONa$

(4) $H_2N{\bigcirc}N{:}N\text{–}HO{\bigcirc}(SO_3Na)NH_2 + 2NaNO_2 + 5HCl$

$\rightarrow ClN{:}N{\bigcirc}N{:}N\text{–}HO{\bigcirc}(SO_3H)N{:}N\text{–Cl} + 3NaCl + 4H_2O$

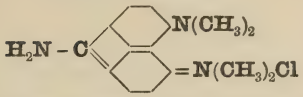
(5) $HO{\bigcirc}OH + ClN{:}N{\bigcirc}N{:}N\text{–}HO{\bigcirc}(SO_3H)N{:}N\text{–Cl} + H_2N{\bigcirc}(CH_3)NH_2 + 3Na_2CO_3$

(resorcinol). (*m*-toluylenediamine).

$\rightarrow HO{\bigcirc}OH{:}N{:}N{\bigcirc}N{:}N\text{–}HO{\bigcirc}(SO_3Na)N{:}N{\bigcirc}(CH_3)(NH_2)NH_2 + 2NaCl + 3NaHCO_3$

(Isodiphenyl black).

15. *Auramine O.*



E.P. 5512[84]; A.P. 301,802[84]; D.P. 29,060[84]; F.P. 160,990[84].

25 grams tetramethyldiamidobenzophenone (Michler's ketone).
25 „ ammonium chloride.
25 „ anhydrous zinc chloride.

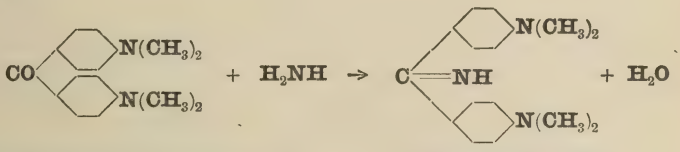
The above quantities are well mixed together in a mortar and transferred to a porcelain dish or jar which has been heated in an oil-bath (temperature of bath, 200°). The mixture gradually melts together and becomes yellow.

The mass is from time to time well stirred, and the temperature of the melt is maintained at 150–160° for four to five hours. The end of the reaction is reached when a test dissolves almost completely in hot water.

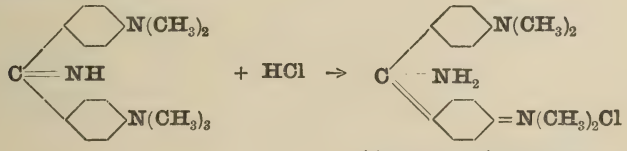
After cooling, the hard mass is finely powdered and treated with cold water containing a little hydrochloric acid, in order to dissolve out the excess of ammonium chloride and zinc chloride. The residue is then extracted with hot water at 60–70°, filtered from any unchanged ketone, and salt added to the filtrate. The crystalline precipitate can be purified by recrystallisation from hot water, the temperature of which must not be over 70°.

Properties.—Sulphur-yellow powder. Dyes silk and tannin-mordanted cotton greenish-yellow.

Equations.—



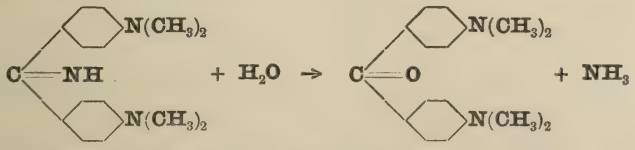
(tetramethyldiamidobenzophenone) (Michler's ketone). (Auramine (base)).



(Auramine (hydrochloride)).

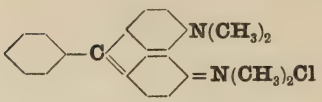
For an explanation of this formula, see p. 77.

Note.—On boiling with water Auramine is slowly hydrolysed according to the equation



Care must be taken, therefore, when dyeing with this colouring matter that the temperature of the dye-bath does not rise above 60–70°, at which temperature the hydrolysis only takes place slowly.

16. *Malachite green.*



(hydrochloride).

E.P. 828[78]; 4762[79];
O. Fischer, *Ber.*, 1877, x. 1625.
O. Mühlhäuser, *Ding. pol. J.*, 1887, celxiii., 249, 295; *J.S.C.I.*, 1887, 433.
Harmsen, *Die Fabrikation*, etc.

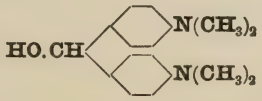
35 grams dimethylaniline.
14 ,, benzaldehyde.

The dimethylaniline and benzaldehyde are mixed with 31·5 grams of concentrated hydrochloric acid and heated in a flask fitted with a reflux condenser at 100° for twenty-four hours. The mass is now made alkaline with caustic soda and treated with a current of steam to remove traces of benzaldehyde and dimethylaniline. On pouring into about 1 litre of water the leuco-base separates in hard granules. It is filtered off and washed free from alkali. A small portion is weighed, dried at 100°, and weighed again in order to calculate the amount of acid and lead peroxide required for the oxidation. For 10 grams of dry leuco-base, hydrochloric acid containing 2·7 grams HCl, 4 grams of acetic acid (10 grams of 40 per cent. or 13 grams of 30 per cent.) and 7·5 grams of pure lead peroxide are required.

(*Preparation of lead peroxide.*—50 grams of lead acetate are dissolved in 250 c.c. of hot water, and a filtered solution of 100 grams of bleaching-powder in 1½ litres of water added. The whole is heated to boiling until the precipitate becomes dark brown. A small quantity is filtered hot and a few drops of bleaching-powder solution added and boiled; if a dark brown precipitate is formed, more bleaching-powder solution is added to the main quantity, and it is heated until a test gives no precipitate with the bleaching-powder solution. After settling, most of the clear liquid is poured off and the precipitate washed several times with water, the wash-waters each time being carefully decanted. The precipitate is now filtered at the pump and washed thoroughly with water. The lead peroxide is transferred, without drying, to a stoppered bottle. Before using the paste, the strength must be determined. See p. 302.)

The requisite quantities having been calculated, the whole of the leuco-base is placed in a porcelain basin, melted by a current of steam and dissolved in the hydrochloric and acetic acids. Two and a half to three litres of water are added, the solution stirred, and a thin paste of the lead peroxide added. Stirring is continued for two hours after all the lead peroxide has been poured in. Unchanged lead peroxide is now filtered off, the filtrate heated to boiling, and lead precipitated by adding sodium sulphate. After filtering, the solution is heated to boiling, and the base precipitated by adding caustic soda. On cooling, it is filtered off, washed, and dried. It is now dissolved in light petroleum (ligroin), the solution filtered from impurities, and the petroleum distilled off by means of a current of steam. The base is melted in 3–4 times its bulk of water, and the requisite amount of oxalic acid (calculated for the formula $2C_{23}H_{24}N_2,3C_2H_2O_4$) added. After filtering the solution, and allowing to cool, the oxalate crystallises out, and is filtered off and dried.

Note.—In the first edition of this book the condensation of benzaldehyde and dimethylaniline was described as being effected by means of zinc chloride as condensing agent. This method is no longer employed on the large scale, but hydrochloric acid is used instead. The amount of acid used is two-thirds of the theoretical amount; more than this quantity gives rise to the production of tetramethyldiamidobenzhydrol

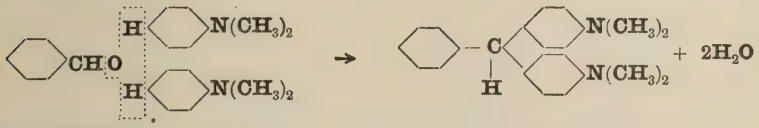


as has been shown by Albrecht (*Ber.*, 1888, xxi. 3292). Instead of the oxalate, the zinc chloride double salt is sometimes prepared, the formula of which is

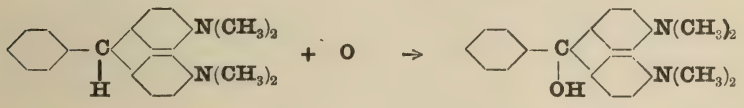
$$3C_{23}H_{25}N_2Cl + 2ZnCl_2 + 2H_2O.$$

Properties.—The oxalate forms green glistening plates, giving a bluish-green solution in water. Dyes silk, wool, jute, and leather a bluish-green; cotton after having been mordanted with tannin and tartar emetic.

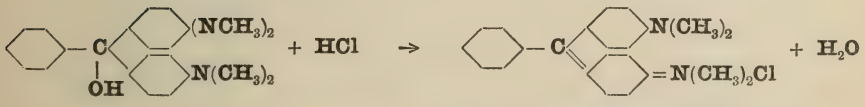
Equations.—



(benzaldehyde). (2 mols.) (dimethylaniline). (leuco-base of Malachite green).



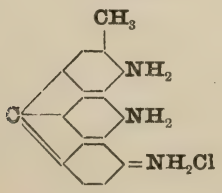
(dye base (carbinol)).



(Malachite green (hydrochloride)).

For an explanation of these formulæ, see p. 88.

17. *Magenta.*



Haüssermann, *Die Industrie der Theerfarbstoffe*, 1881.
Harmsen, *Die Fabrikation der Theerfarbstoffen und ihrer Rohmaterialien*, 1889.
Schultz, *Chemie des Steinkohlentheers*, 3rd ed., vol ii. p. 161.

20 grams	aniline.		
80 „	commercial toluidine	{ 64 per cent. *ortho* 36 „ „ *para* }	Aniline oil for red, sp. gr. 1·004.
67 „	conc. hydrochloric acid.		
55 „	nitrobenzene.		
3 „	iron powder.		

Fourteen grams of aniline and 54 grams of the toluidine are mixed together in a porcelain basin and the hydrochloric acid added. The mixture of hydrochlorides is heated till the temperature is 130°, when it is transferred to a round flask of one-quarter-litre capacity, in which has been placed the rest of the aniline and toluidine together with the nitrobenzene.

The mixture is heated in an oil-bath to 100°, when the iron, dissolved in 2 mols. of HCl (to form $FeCl_2$), is slowly added.

The flask is now connected with an air-condenser and the temperature raised gradually to 180°, which is maintained for six to eight hours. The melt is finished when a sample withdrawn on a glass rod solidifies on cooling.[1]

When this point is reached the contents of the flask are distilled with steam, when a mixture of red oil and nitrobenzene passes over. The melt is now poured into 500 c.c. of boiling water, well stirred, and 12 c.c. concentrated hydrochloric acid added slowly. As soon as an acid reaction has been obtained, 25 grams of salt are added, and the whole boiled for a few minutes.

The aqueous solution which is poured off contains the hydrochloride of aniline and toluidine, which, as well as the previous distillates, is, on the large scale, used again in the manufacture (see also *Safranine*). The residue is allowed to cool, and solidifies to a green, brittle mass, which is weighed.

This is then broken up and extracted with 1½ litres of boiling water containing 12 c.c. of HCl, which dissolves the Magenta. After filtering, the solution is allowed to cool to 60°, when a little violet colouring matter separates out, which is filtered off.

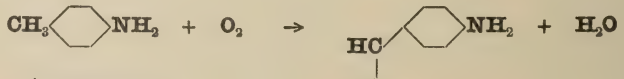
Salt is now added to the Magenta solution, the weight being the same as the weight of the crude melt. After standing some time the crude Magenta separates out, is filtered off, and recrystallised from water containing a little hydrochloric acid.

The filtrates from the purification of Magenta are, on the large scale, worked up, and the colouring matters obtained from them sold under the names of Phosphine, Maroon, Cerise, etc.

Properties.—The hydrochloride forms glistening crystals with a greenish reflection, dissolving in water to a red solution.

Dyes silk and wool bluish-red direct; cotton, after having been mordanted with tannin and tartar emetic.

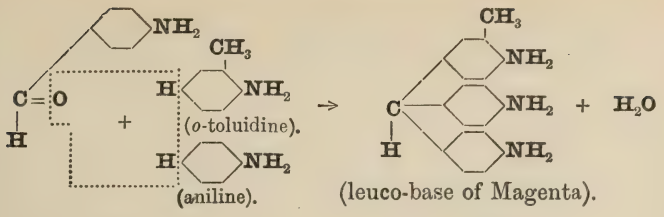
Equations.—

(1) 

(*p*-toluidine). (*p*-amidobenzaldehyde).

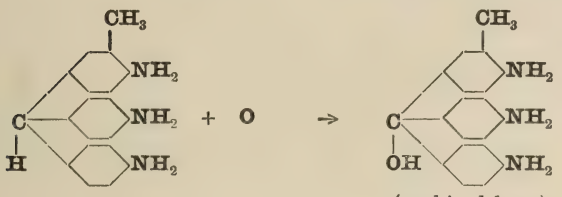
[1] Begin to test after three and a half hours—three to four hours may be sufficient.

(2)



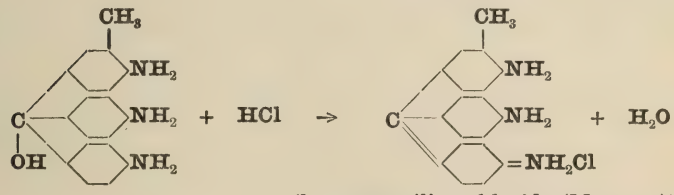
(leuco-base of Magenta).

(3)



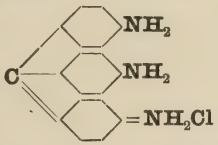
(carbinol base).

(4)



(homorosaniline chloride (Magenta)).

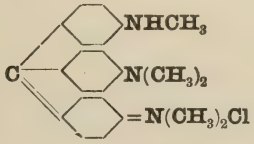
At the same time there is also formed



(*para*-rosaniline chloride),

owing to the interaction of 2 mols. of aniline in equation (2) instead of 1 mol. of aniline and 1 of *o*-toluidine.

18. *Methyl violet B.*



Mühlhaüser, *Dingl. pol. J.*, 1887, cclxiv. 37; *J.S.C.I.*, 1887, 434. Harmsen, *Die Fabrikation*, etc.

875 grams sodium chloride.
50 ,, copper sulphate.
40 ,, phenol.
100 ,, dimethylaniline.

The salt and copper sulphate (finely powdered) are well mixed together in a mortar, and a solution of 40 grams of phenol in 10 c.c. of water added, and the whole stirred well. The dimethylaniline is now added, and the mixture transferred to a round flask and heated on the water-bath for eight hours at 55°. The product is poured out into a porcelain basin and allowed to cool.

In order to free it from phenol and salt, it is broken up and added gradually to 3 litres of boiling water, to which has been added milk of lime prepared from 40 grams of quicklime and 200 c.c. of water. After heating till no more lumps are present, the mixture is allowed to settle, and the clear solution of salt and calcium phenate decanted.

The residue of copper oxide, methyl violet, and calcium sulphate is washed again by decantation and finally filtered.

In order to get rid of the copper oxide the precipitate is boiled with dilute sulphuric acid, and sodium sulphate (free from chloride) added to precipitate the dye, which is filtered and washed. The precipitated violet is subsequently dissolved in water and reprecipitated with salt.

Properties.—Methyl violet is a glistening greenish powder, dissolving in water with a violet colour.

Dyes silk and wool violet direct; cotton, after mordanting with tannin and tartar emetic.

Equations.—

(1) $C_6H_5N(CH_3)_2 + O \rightarrow CH_2O + C_6H_5NH(CH_3)$

(2) $H-C(=O)-C_6H_4NH(CH_3) + C_6H_4N(CH_3)_2 + C_6H_4N(CH_3)_2 + 2O \rightarrow C(OH)(C_6H_4NH(CH_3))(C_6H_4N(CH_3)_2)(C_6H_4N(CH_3)_2) + 2H_2O$

(carbinol base).

(3) $C(OH)(C_6H_4NH(CH_3))(C_6H_4N(CH_3)_2)(C_6H_4N(CH_3)_2) + HCl \rightarrow C(Cl)(C_6H_4NH(CH_3))(C_6H_4N(CH_3)_2)(C_6H_4=N(CH_3)_2Cl) + H_2O$

(Methyl violet B (hydrochloride)).

19. *Aniline blue* (spirit soluble) or *Opal blue.*

$C(C_6H_4NHC_6H_5)(C_6H_4NHC_6H_5)(C_6H_4=NHC_6H_5Cl)$

J. de Mollins, *De la fabrication des Bleus d'aniline et de diphénylamine*, 1885.

25 grams rosaniline base (prepared from Magenta).[1]
250 „ aniline.
3 „ benzoic acid.

[1] By boiling with caustic soda solution.

The above quantities are placed in a flask provided with a thermometer, and a long bent tube to collect a small amount of aniline, ammonia, and water, which distils over during the operation. The flask is heated slowly on a sand-bath to 180°, and maintained at this temperatnre until a few drops dissolved in alcohol and a little glacial acetic acid and poured on filter-paper show a pure blue colour by daylight, which is only tinged slightly red in gaslight. This operation requires about three hours. The hot melt is then poured into a beaker, allowed to cool a little, and 215 grams of hydrochloric acid, 28 per cent. (or 194 grams of pure concentrated acid, 31 per cent.), added. The Opal blue is thus precipitated, whilst an impure blue remains dissolved in the mixture of aniline and aniline hydrochloride (formed by the partial neutralisation of the aniline). The mixture is filtered hot at the pump, and the Opal blue washed with boiling water to which a few drops of hydrochloric acid have been added. The colouring matter is dried on the water-bath. It is thus obtained in the form of a greenish or reddish brown crystalline powder. Yield about 30 grams.

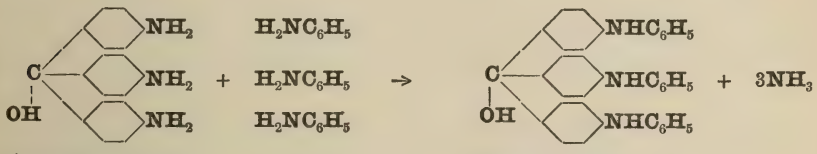
The filtrate containing the impure blue is acidified with hydrochloric acid, whereby the colour is precipitated, and is filtered, washed as above, and dried. Yield about 15 grams of impure blue (dyeing duller and redder shades than the Opal).

Both the shade and the yield depend largely on the length of time during which the heating is carried on. Care must be taken not to allow the temperature to rise above 180°.

Properties.—Insoluble in water, but soluble in alcohol. Dyes silk and wool greenish-blue.

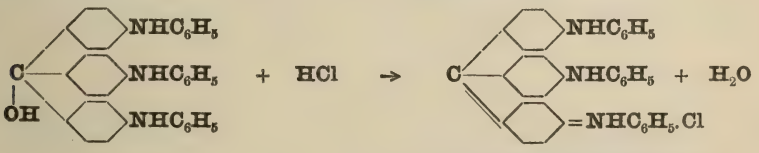
Equations.—

(1)



(rosaniline base). (Rosaniline blue) (base).

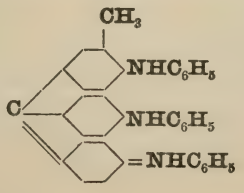
(2)



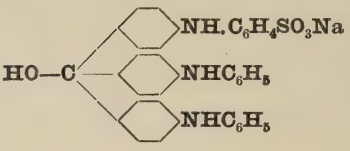
(Aniline blue (spirit sol.) hydrochloride).

(See p. 92.)

Owing to Magenta being a mixture of *para-* and *homo*-rosaniline, there will also be formed in this reaction a blue of the formula



20. *Alkali blue.*



25 grams Aniline blue (spirit soluble).
250 „ conc. sulphuric acid (140 c.c.).

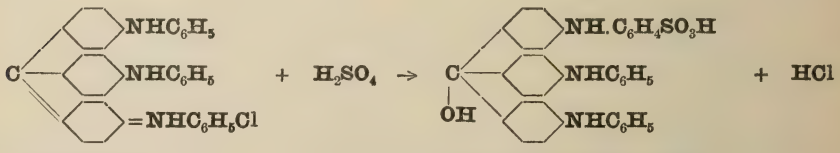
The sulphuric acid is placed in a 500-c.c. flask, and the Aniline blue, which is obtained from the melt in the form of a fine crystalline powder, is slowly added, keeping the temperature below 35°. The experiment should be conducted in the draught cupboard, as hydrochloric acid is evolved.

When all the blue is dissolved, the temperature is maintained at 35–40° until a few drops diluted with water and filtered yield a residue which dissolves in a weak boiling solution of caustic soda. The sulphonation mixture is then poured into about 2 litres of cold water, filtered at the pump, and the precipitate washed with water until free from acid. The moist free acid thus obtained is transferred to a porcelain basin, made into a thin paste with hot water, and converted into the sodium salt by the cautious addition of caustic soda solution, the whole being heated to boiling. If the correct amount of caustic soda has been added, a sample will dissolve completely, in hot water, with a blue colour. Should, however, an excess of alkali be present, the colour will be brown, and in this case a weak solution of sulphuric acid is stirred slowly into the hot mixture until the right point is reached. The solution is then evaporated nearly to dryness on the water-bath, and finally dried at 50°.

Properties.—Blue or bronzy powder, sparingly soluble in cold, easily in hot water with a blue colour. Dyes wool blue from a boiling bath made alkaline with borax, the colour being subsequently developed by passing through weak sulphuric acid.

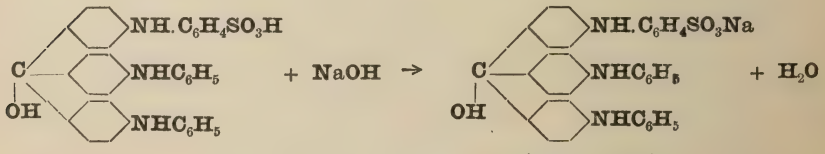
Equations.—

(1)



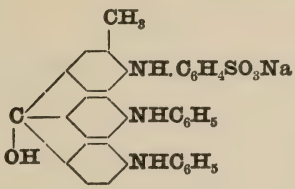
(Rosaniline blue). (Alkali blue) (free acid).

(2)



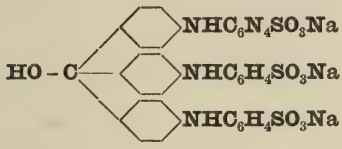
(Alkali blue).

This product will also be mixed with the corresponding homorosaniline derivative



See previous preparation.

21. *Soluble blue.*



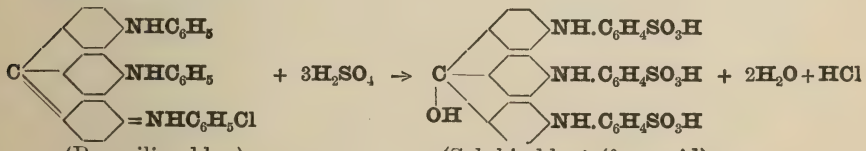
25 grams Aniline blue (spirit soluble).
100 „ conc. sulphuric acid (55·5 c.c.).

The blue is gradually added to the acid contained in a flask, and the whole heated on a sand-bath up to 90–100°, until a sample poured into a little water and filtered is soluble in warm water. The sulphonation mixture is now poured into about 500 c.c. of cold water and filtered at the pump. The precipitated colouring matter is washed only with a little water, as it is soluble in pure water. It is transferred to a basin, a little water added, and the mixture heated to nearly boiling, then neutralised with caustic soda solution until the whole is soluble with a blue colour.

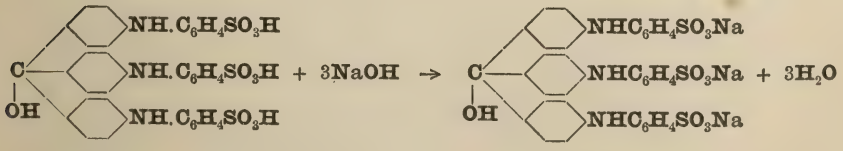
If the mixture turns brown there is too much alkali present, and this must be neutralised by the cautious addition of weak sulphuric acid. It is evaporated to dryness on the water-bath and ground. Yield about 30 grams.

Properties.—Blue powder, soluble in water. Dyes silk and mordanted cotton, blue.

Equations.—

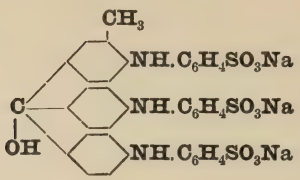


(Rosaniline blue). (Soluble blue) (free acid).



(Soluble blue).

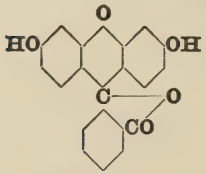
This blue will also be accompanied by the corresponding homorosaniline derivative



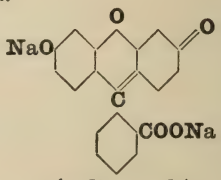
Fluoresceïn and Eosine.

Mühlhäuser, *Dingl. pol. J.*, 1887, cclxiii. 49; *J.S.C.I.*, 1887, 283; *Dingl. pol. J.*, 1892, cclxxxiv. 21, 46; *J.S.C.I.*, 1892, 675.
Bernthsen, *Chem. Zeit.*, 1892, xvi. 1956; *J.S.C.I.*, 1893, 513.

22. *Fluoresceïn.*



(free acid).

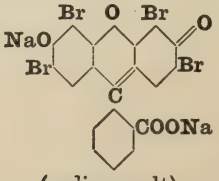


(sodium salt).

15 grams phthalic anhydride.
22 „ resorcinol.
7 „ zinc chloride.

The materials are ground together in a mortar, transferred to a nickel crucible or similar vessel, and heated in an oil bath to 180°. As soon as the temperature has reached 180°, 7 grams of powdered fused zinc chloride are added gradually during ten minutes, the melt being stirred with a glass rod. After the zinc chloride has been added the temperature is raised to 210°, and kept at this point till the mass becomes solid (one to two hours). The cold melt is broken out of the crucible or jar with a knife or chisel, powdered, and dissolved in dilute caustic soda. After filtering, hydrochloric acid is added, which precipitates the fluoresceïn; this is filtered, washed, and dried. Yield about 32 grams.

23. *Eosine.*



(sodium salt).

15 grams fluoresceïn.
33 „ bromine (11 c.c.).
60 „ alcohol.

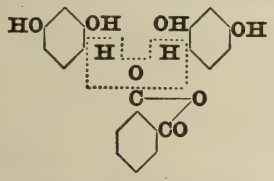
The fluoresceïn is placed in a flask, 60 grams of alcohol added, and the bromine dropped in slowly from a small separating funnel. When half the bromine has been added, the dibromide which is formed is in solution; but on further addition of bromine, the tetrabromide separates out. After standing for two hours the precipitate is filtered, washed first with alcohol, then with water, and converted into the sodium salt by mixing it with a little hot water, carefully neutralising with caustic soda (avoiding an excess of this reagent), and evaporating to dryness on the water-bath.

Properties.—Eosine forms bluish-red crystals or a brownish-red powder, dissolving in water with a bluish-red colour.

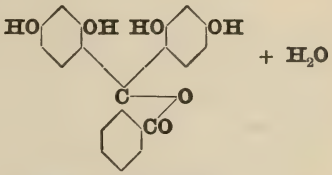
Dyes wool and silk yellowish-red.

Equations.—

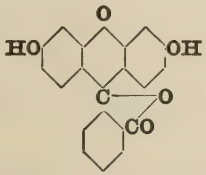
(resorcinol). (resorcinol).



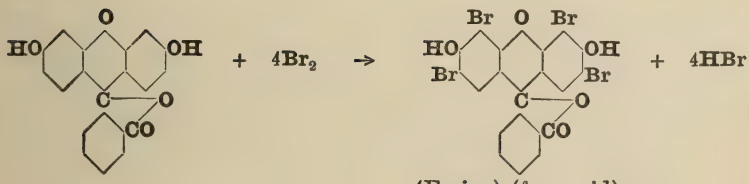
(phthalic anhydride).



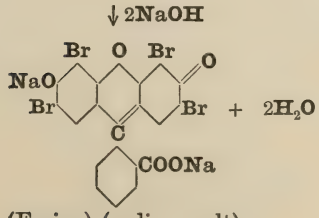
(resorcinphthaleïn).



(Fluoresceïn) (free acid).



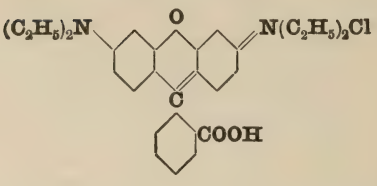
(Eosine) (free acid).



(Eosine) (sodium salt).

For a further explanation of these formulæ, see p. 109.

24. *Rhodamine B.*



E.P. 15,374[87]; A.P. 377,349 and 377,350[88]; D.P. 44,002[87]; F.P. 186,697[87].

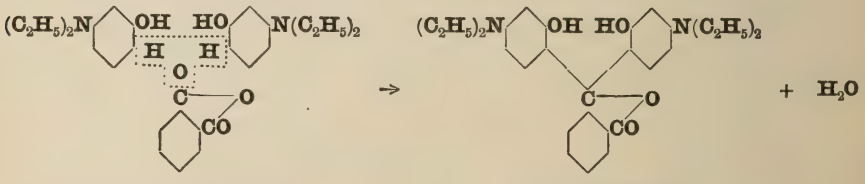
5 grams diethyl-*meta*amidophenol.
9 ,, phthalic anhydride.
6 ,, anhydrous zinc chloride.

The two first are well mixed together in a mortar and the mixture transferred to a nickel crucible, which is heated in an oil-bath. The temperature is raised slowly to 100°, the flame withdrawn, and the powdered zinc chloride added, the whole being well stirred. The temperature is then raised gradually to 180°, water vapour is given off, and the reaction is finished when a sample withdrawn by a glass rod completely solidifies on cooling. This takes about four to five hours. The solid product, when cold, is finely powdered and extracted with boiling alcohol on a reflux condenser. The alcoholic solution is filtered and allowed to stand. The colour-base crystallises out and is filtered. The base is dissolved in a small quantity of water and dilute hydrochloric acid, and the solution allowed to cool, when the hydrochloride separates out, and is filtered, and dried on a porous plate.

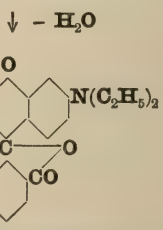
Properties.—Green crystals, easily soluble in water. Dyes wool and silk bluish-red, tannin-mordanted cotton violet-red.

Equations.—

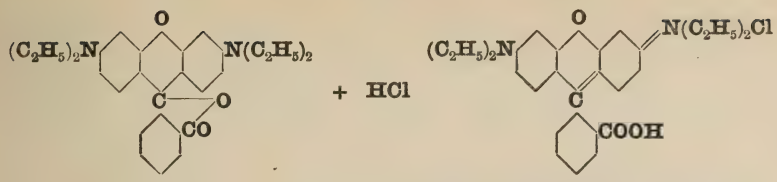
(Diethyl-*m*-amidophenol).



(phthalic anhydride). (the phthaleïn).



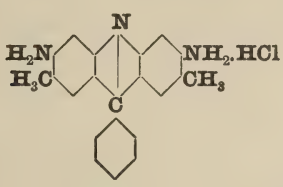
(Rhodamine) (base).



(Rhodamine B) (hydrochloride).

For an explanation of these formulæ, see p. 109.

25. *Benzoflavine.*



E.P. 9614[88]; A.P. 382,832; D.P. 43,714[87]; 43,720[87].

I. Preparation of tetramidophenylditolylmethane.—

20 grams metatoluylenediamine sulphate.[1]
5·5 „ benzaldehyde.
40 „ alcohol, 50 per cent.

These are mixed together in a round flask of 125-c.c. capacity, fitted with a reflux condenser, and gently boiled on the water-bath. When the smell of benzaldehyde is no longer present, the alcohol is distilled off, and water added to the residue; the sulphate of the above base is filtered and dried.

II. Preparation of dihydrodiamidodimethylphenylacridine.—20 grams of the crude sulphate prepared as above are heated with 36 grams of concentrated hydrochloric acid and 36 c.c. of water in a sealed tube (larger quantities may be heated in an autoclave) for three hours to 130–140°. After cooling, the tube is opened and the product used directly, without purification.

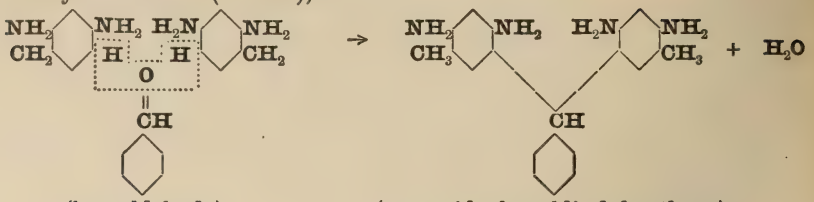
III. Preparation of the colouring matter.—20 grams of the hydrochloride of dihydrodiamidodimethylphenylacridine are dissolved in water containing hydrochloric acid, the solution cooled to 0°, and 20 grams of zinc chloride, dissolved in a little water, added. The solution is stirred and 70 grams of an ice-cold 30 per cent. solution of ferric chloride ($FeCl_3.6H_2O$) added. The colouring matter separates out as a voluminous orange-yellow precipitate, which is filtered, pressed on a porous plate, and dried at 50–60°.

Properties.—Brownish orange-yellow powder. Dyes silk, wool, and mordanted cotton yellow.

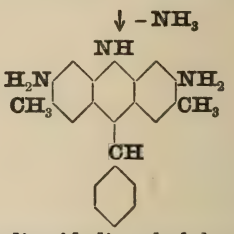
[1] This is obtained by neutralising a strong solution of metatoluylenediamine in hot water with dilute sulphuric acid, when the sulphate crystallises out on cooling.

Equations.—

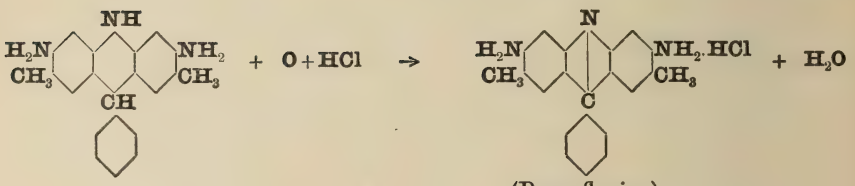
(*m*-toluylenediamine (2 mols.)).



(benzaldehyde). (tetramidophenylditolylmethane).

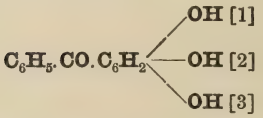


(dihydrodiamidodimethylphenylacridine).



(Benzoflavine).

26. *Alizarine yellow A.*



E.P. 8373[89], 9428[89], 10,095[90]; A.P. 198,281[89]; D.P. 49,149[89], 50,450[89], 50,451[89], 54,661[90]; F.P. 198,281[89].

12 grams pyrogallic acid.
12 „ benzoic acid.
36 „ anhydrous zinc chloride.

The above quantities are mixed together and put in a 200-c.c. crucible or jar, which is heated in an oil-bath. The temperature is gradually raised to 145°, and the reaction is finished when there is no more foaming and the brown colour does not increase.

The cold product is powdered and boiled with water and a little animal charcoal and filtered; the needle-shaped crystals of the dyestuff separate out on cooling, which are filtered and dried.

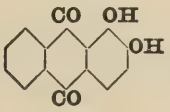
Properties.—Greyish-yellow crystals. Dyes cotton, mordanted with alumina and lime, a fast golden yellow. It is used for printing.

Equation.—

$C_6H_5CO.OH + H.C_6H_2(OH)_3[1:2:3] \rightarrow C_6H_5.CO.C_6H_2(OH)_3[1:2:3] + H_2O$

(benzoic acid). (pyrogallic acid). (Alizarine yellow A).

27. *Alizarine.*



E.P. 1936[69]; A.P. 153,536.
Perkin, E.P. 1948[69], *J.S.C.I.*, 1883, 213.

50 grams sodium anthraquinone sulphonate.
150 „ sodium hydrate.
9 „ potassium chlorate.

The caustic soda is dissolved in 150 c.c. of water in an autoclave, and the sodium anthraquinone sulphonate stirred in. The potassium chlorate is dissolved in 50 c.c. of hot water and thoroughly mixed with the mass.

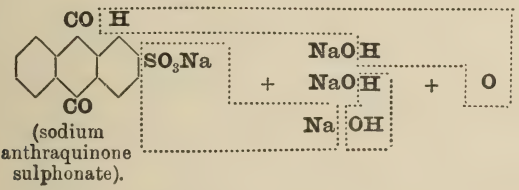
The lid of the autoclave is then fixed on and the whole heated for twenty hours to 170°. After cooling, the melt is extracted with boiling water several times, and the solution acidified with hydrochloric acid.

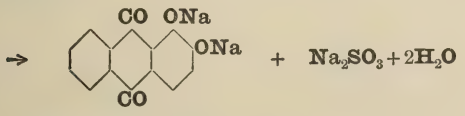
The alizarine which separates out is filtered at the pump, washed with water, pressed on a porous plate, and dried at 120°.

Properties.—Yellow powder, slightly soluble in boiling water; can be sublimed to long red needles. Dyes cotton, mordanted with alumina, scarlet-red; with tin, bluish-red; with iron, violet; with chromium, brown.

Equation.—

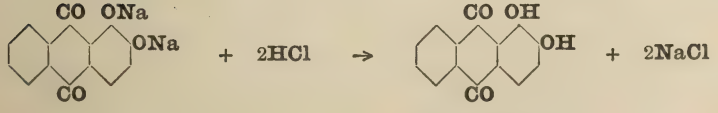
(1)





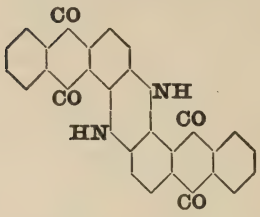
(sodium salt of Alizarine).

(2)



(Alizarine).

28. *Indanthrene A.*



Scholl and Berblinger, *Ber.*, 1903, xxxvi. 3428; E.P. 3239[01], 12,185[01], A.P. 682,523.

50 grams 2-amidoanthraquinone.
250 ,, caustic potash.
10 ,, potassium nitrate.

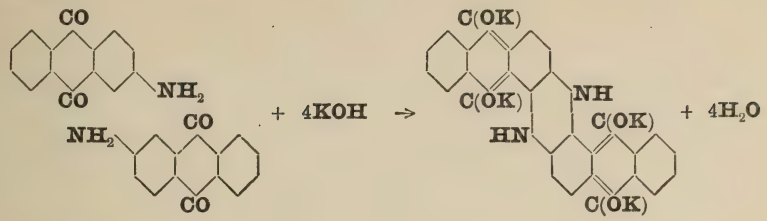
The caustic alkali is placed in a nickel dish suspended in an anthracene bath, and is rendered liquid by the addition of a little water. The temperature is then raised gradually to 200°, at which point the potassium nitrate and subsequently the 2-amidoanthraquinone are added, the whole being well mixed by stirring. The temperature is then raised to 250° and maintained at this point for half an hour, when the melt is cooled, ground to powder, and boiled with water. The precipitated colouring matter is then filtered and washed.

As already mentioned (see p. 128), Indanthrene formed in this manner contains a small quantity of Indanthrene B, a substance valueless as a dyestuff. Purification can be effected by taking advantage of the difference in solubility of the hydro derivatives in dilute alkali, and can be carried out in the following way:—50 grams of crude Indanthrene in the form of paste is diluted with 5 litres of water and warmed to 60–70°. 100 grams of a 25 per cent. solution of caustic soda mixed with 750 grams of sodium hydrosulphite solution (sp. gr. 1·074) are then added, and the temperature maintained at 60–70° for one hour. At the end of this time the colouring matter will have completely passed into solution, from which, on cooling, and keeping for some hours, the sodium salt of the dihydro derivatives of Indanthrene A will separate as well-formed needles with copper reflex. These are then collected by filtration, washed with a little dilute alkali containing some hydrosulphite, and converted into pure Indanthrene A by dissolving in warm water and passing air into the solution. The brown-red mother liquor contains the more soluble hydro derivative of Indanthrene B, and this substance separates as a bluish-green flocculent precipitate when air is passed into the solution.

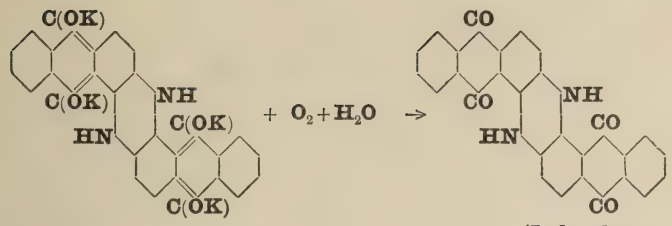
Properties.—Indanthrene A prepared in this manner is a dark powder with strong metallic reflex. It is practically insoluble in the usual organic solvents, but is sparingly soluble in boiling aniline and in nitrobenzene, in the latter case to the extent of about 1 part in 5000. It dissolves (1 part in 500) in boiling quinoline, forming a blue solution from which the colouring matter separates on cooling as characteristic curved needles which resemble indigo in appearance. When heated it partly sublimes in the form of its curved needles, and chars at between 470–500°. Cotton is substantively dyed blue in the vat prepared by the reduction of Indanthrene with sodium hydrosulphite. The dihydro derivative is reconverted into Indanthrene when the dyed fibre is exposed to the air.

Equations.—

(1)

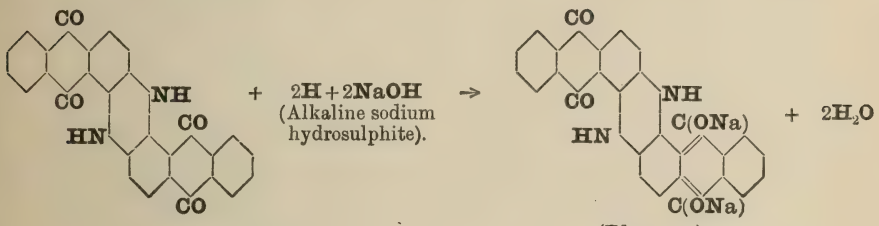


(2)



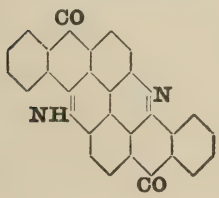
(Indanthrene A).

The blue vat of Indanthrene contains the disodium salt of the dihydro derivative, and is formed as follows:—



(Blue vat).

29. *Flavanthrene.*



Scholl, *Ber.*, 1907, xl. 1694; E.P. 24,354[01], A.P. 739,145.

10 grams 2-amidoanthraquinone.
35 „ anhydrous antimony pentachloride.
100 „ nitrobenzene.

The amidoanthraquinone is added gradually to the solution of antimony pentachloride in nitrobenzene at 60–80°, and the mixture is kept at the boiling-point for one hour; the containing flask being without condenser.

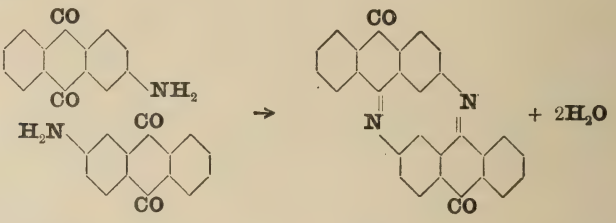
Chemically pure Flavanthrene separates as brown-yellow needles when the

solution is cooled, and can be isolated by filtration. It is subsequently washed on the filter with nitrobenzene and then with ether.

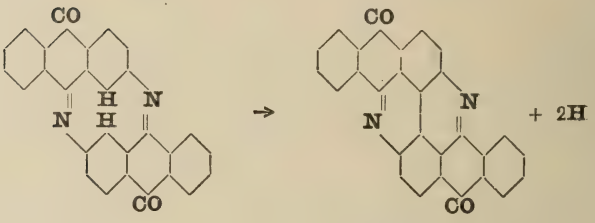
Properties.—Flavanthrene is practically insoluble in all the usual organic solvents. One kilogram of quinoline dissolves about 2 grams of the colouring matter after boiling for 1–2 hours, and when cooled reprecipitates it as glistening brown-yellow needles. The hydrosulphite vat is violet blue, and cotton, which is dyed blue in this vat, changes to the yellow of Flavanthrene when exposed to the air.

Equations.—

(1)

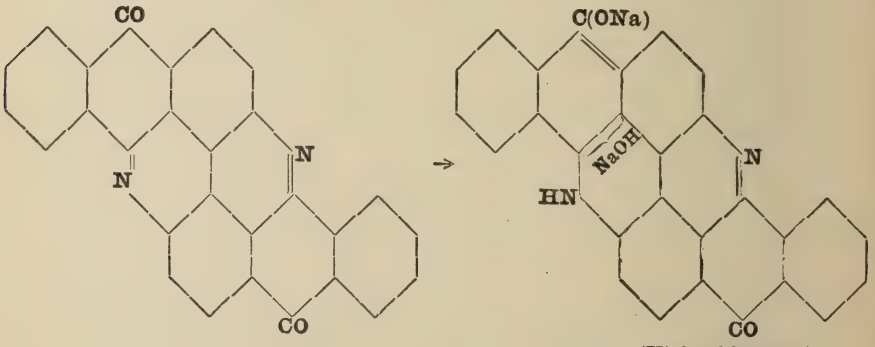


(2)



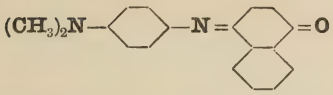
(Flavanthrene).

The violet blue vat of Flavanthrene contains the disodium salt of the dihydro derivative formed by the action of sodium hydrosulphite as follows:—



(Violet blue vat).

30. *Indophenol.*



E.P. 1373[81], 5249[81]; A.P. 261,518; D.P. 15,915[81], 18,903[81], 19,231[81], 20,850[81].
J.S.C.I., 1882, i. 255.

10 grams nitrosodimethylaniline hydrochloride.
10 „ zinc dust (sieved).
12 „ α-naphthol.
3·3 „ caustic soda.
10 „ potassium bichromate.

The nitroso-compound is dissolved in 1 litre of water and reduced by adding the zinc dust and warming the solution to 45–50°. The mixture becomes colourless, and is filtered from the zinc and zinc oxide.

The solution of amidodimethylaniline is mixed with the naphthol solution prepared by dissolving the naphthol in 3·3 grams of caustic soda and a little water, and to this is added the solution of bichromate in 200 c.c. of water.

The mixture is well stirred mechanically, and ordinary acetic acid, 30 to 40 per cent., is slowly added till an acid reaction is obtained. The dye is formed and is precipitated.

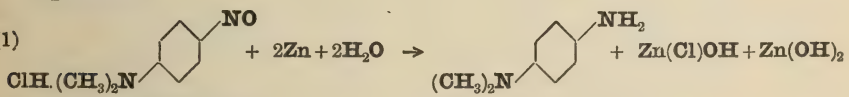
This is filtered, washed, and dried.

Properties.—Indophenol is a dark brown powder, insoluble in water.

Use.—Indophenol is converted into the leuco-compound by reduction with stannous chloride or acetate, which is then used for printing and dyeing in the same way as Indigo.

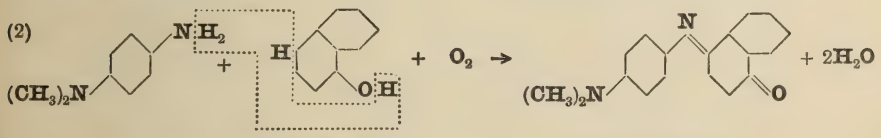
Equations.—

(1)



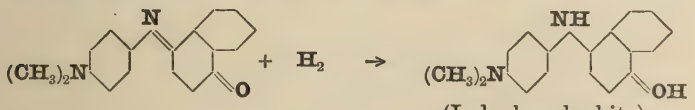
(nitrosodimethylaniline) (hydrochloride). (dimethyl-*p*-phenylene-diamine).

(2)



(α-naphthol). (Indophenol).

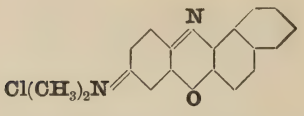
On reduction Indophenol is converted into Indophenol white



(Indophenol white),

in which condition it is soluble in alkali, and then possesses affinity for the fibres upon which it can be reconverted into the blue on oxidation in the air.

31. *Meldola's blue* (*Naphthol blue*)



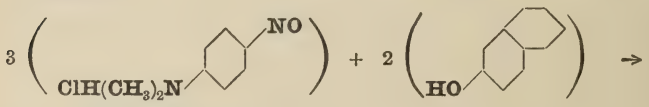
Meldola, *Ber.*, 1879, xii. 2065; *J.C.S.*, 1881, xxxix. 37.
Witt, *Ber.*, 1890, xxiii. 2247.
Meldola, *Private communication.*

21 grams β-naphthol.
53 ,, nitrosodimethylaniline hydrochloride.

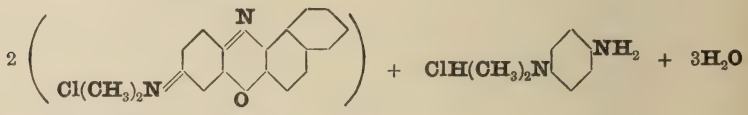
The above quantities are dissolved in alcohol and heated on the water-bath in a round flask, fitted with a reflux condenser, for a day. The colouring matter is formed, and is separated by adding a solution of zinc chloride until no further precipitate is obtained. The zinc chloride double salt is filtered and dried on a porous plate. Yield 30 grams.

Properties.—Dark violet powder, soluble in water with bluish-violet colour. Dyes cotton, mordanted with tannin and tartar emetic, indigo blue.

Equation.—

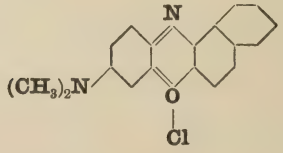


(nitrosodimethylaniline) (hydrochloride). (β-naphthol).

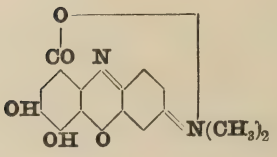


(Meldola's blue).

The formula of this substance, as a derivative of *o*-quinone containing tetravalent oxygen, would be



32. *Gallocyanine.*



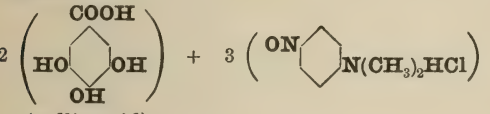
E.P. 4899[81]; A.P. 253,721 and 257,498; D.P. 19,580[81].

10 grams gallic acid.
17 „ nitrosodimethylaniline hydrochloride.
200 c.c. alcohol, 95 per cent.

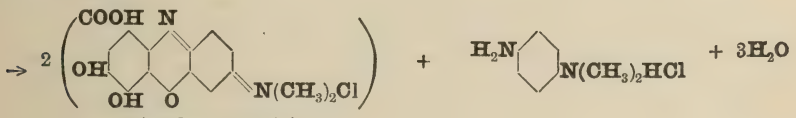
The above quantities are mixed together in a 500-c.c. round flask fitted with a reflux condenser, and heated on the boiling water-bath. The course of the reaction is observed by spotting a drop on filter-paper and observing the colour. When this is dark violet-blue, and does not change on further heating the flask, the reaction is finished. There must also be no yellow rim round the drop of colour on the filter-paper. The alcohol is distilled off on the water-bath and the residue evaporated to dryness. This is boiled with 200 c.c. of water, filtered, and dried on a porous plate, and finally at 40–50°.

Properties.—Bronze powder, insoluble in water. Dyes chrome-mordanted wool bluish-violet, and is used in printing upon chrome-mordanted wool and cotton.

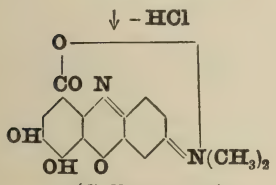
Equations.—



(gallic acid).

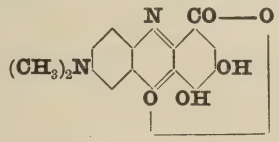


(hydrochloride).



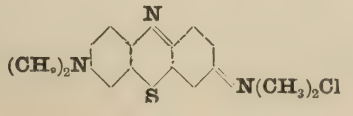
(Gallocyanine).

The formula of this substance would be represented by



on the assumption that the oxazine salts are derivatives of *o*-quinone containing tetravalent oxygen (see p. 141).

33. *Methylene blue.*



E.P. 43[86]; D.P. 38,573[85], 39,757[86]; A.P. 362,592, 366,639, 366,640, 384,480; F.P. 173,137, 181,827.

24 grams dimethylaniline.
65 „ conc. hydrochloric acid.
7·1 „ sodium nitrite.
20 „ zinc dust.
50 „ sodium thiosulphate.
25 „ potassium bichromate.
53 „ sulphuric acid.
8 „ neutral sodium chromate.

Twelve grams of dimethylaniline are dissolved in a mixture of 40 c.c. of water and 65 grams of concentrated hydrochloric acid, and the solution cooled with ice to 12–15°. This is stirred mechanically, and a solution of 7·1 grams of sodium nitrite run in slowly (delivery tube underneath the surface of the liquid), taking care that the temperature does not rise above 15°. The nitroso-compound is reduced by adding about 20 grams of zinc dust carefully, and the reduction is complete when the solution is of a clear red colour. The amount of zinc added must be sufficient to neutralise the hydrochloric acid, so that Congo paper is no longer turned blue. The solution is now diluted with water to 500 c.c., and a solution of 12 grams of dimethylaniline in the exact quantity of hydrochloric acid necessary to form the hydrochloride (about 10 c.c.) added, and then a solution of 50 grams of sodium thiosulphate in a little water.

The mixture is oxidised by adding a concentrated solution of 25 grams of potassium bichromate and boiling for two hours.

Fifty-three grams of sulphuric acid first diluted with 100 c.c. of water are now added, and the solution boiled to expel SO_2.

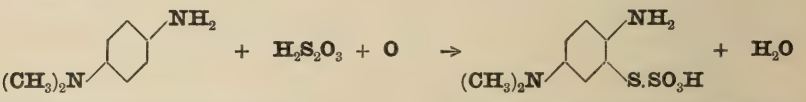
The leuco-methylene blue is oxidised by adding 8 grams of neutral sodium chromate dissolved in a little water, and the resulting dye is precipitated by adding salt.

The base is filtered, dissolved in a little boiling water to which a little hydrochloric acid has been added, and the hydrochloride precipitated by common salt, filtered, and dried on a porous plate.

Properties.—Dark green or red-brown bronzy powder, easily soluble in water, forming a blue solution. Dyes tannin-mordanted cotton blue.

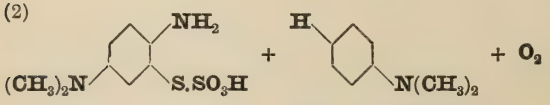
Equations.—

(1)

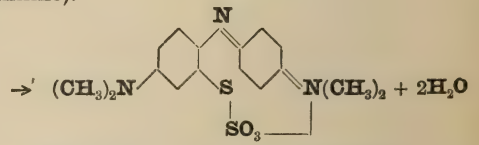


(dimethyl-*p*-phenylenediamine). (thiosulphonic acid of dimethyl-*p*-phenylenediamine).

(2)

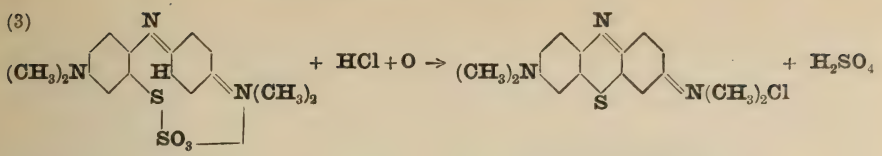


(dimethylaniline).



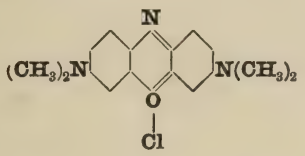
(thiosulphonic acid of an indamine).

(3)

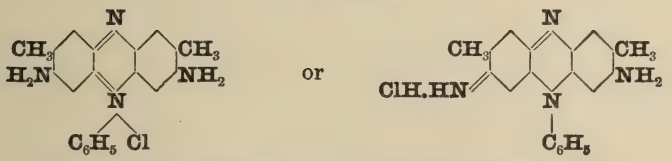


(Methylene blue).

This substance, formulated as an *o*-quinone derivative containing tetravalent oxygen, would be



34. *Safranine.*



Walter, *Aus der Praxis der Anilinfarbenfabrikation.*

24 grams *o*-toluidine.
30 „ granulated tin.
20 „ zinc dust.
9·5 „ aniline.
40 „ potassium bichromate.

I. Preparation of amidoazotoluene.—The toluidine is mixed with 14·5 grams of concentrated hydrochloric acid (12·5 c.c.) in a small thick beaker, and the mixture cooled under the tap to 18–20°. 7·8 grams of powdered sodium nitrite are now added very gradually, whereby the temperature rises to 33°. If the nitrite be added too quickly, the temperature may rise to 60° or 70° and the experiment is spoiled. After stirring for one-quarter of an hour longer the amidoazotoluene is filtered, washed once with a little water, and left standing for two days before use. (This is done in order that the last traces of diazoamidotoluene may be completely converted into amidoazotoluene.)

II. Reduction.—30 grams of granulated tin are mixed with 80 grams of concentrated hydrochloric acid (69 c.c.), and the powdered amidoazotoluene added to the mixture slowly, during which operation the temperature may rise to 70°. When the liquid has become clear and no more lumps of amidoazotoluene are present, cold water is added till the temperature is brought down to about 60°, and the tin in solution is precipitated by zinc. For this purpose 15–20 grams of zinc dust are stirred up with 25 c.c. of water and added gradually to the reduction mixture. The temperature should not be allowed to rise above 80°.

The precipitation of the tin must be complete. In order to test this a few drops of the mixture are filtered, acidified with dilute hydrochloric acid, and sulphuretted hydrogen passed through; this should produce no dark colour, otherwise more zinc dust must be added to the above mixture.

The mass is now filtered hot, the residue of tin washed with hot water, and to the united filtrates is added 9·5 grams of aniline dissolved in 10 c.c. of concentrated

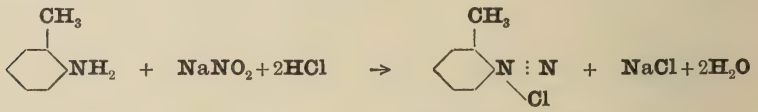
hydrochloric acid and 75 c.c. of water. (On the large scale the liquid at this point is tested by titration with a 10 per cent. solution of potassium bichromate till no more blue colour is formed (indamine), and from the amount of bichromate used, the quantity of aniline is calculated.

III. Oxidation.—For the oxidation, 40 grams of potassium bichromate are dissolved in water and added to the above mixture. (On the large scale regained manganese dioxide is now used, containing 65 to 68 per cent. MnO_2). A blue precipitate is at once formed, and the whole is boiled, when the blue colour gradually changes to red. When no further change of colour takes place (seen by spotting on filter-paper), the mixture is filtered hot, the residue washed with hot water, and the filtrate, containing the safranine, salted, whereby the dye is precipitated. After cooling, this is filtered and dried at 100°

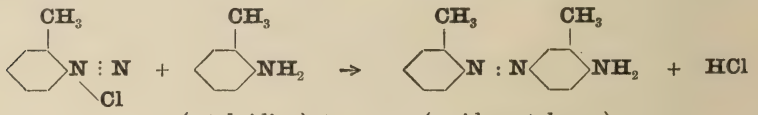
The residue, which contains bluer colouring matters, is on the large scale worked up for these.

Properties.—Reddish-brown powder, soluble in water with a red colour. Dyes cotton, mordanted with tannin and tartar emetic, red.

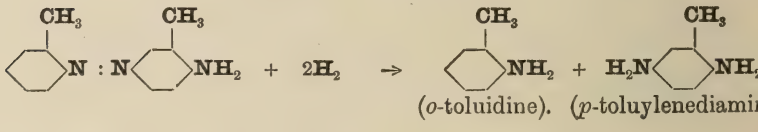
Equations.—

(1) 

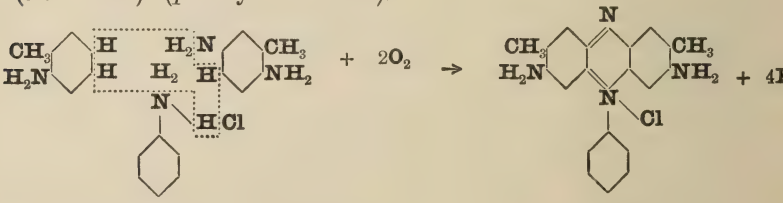
(*o*-toluidine). (diazo-compound).

(2) 

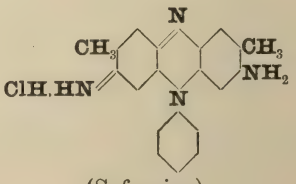
(*o*-toluidine). (amidoazotoluene).

(3) 

(*o*-toluidine). (*p*-toluylenediamine). (*o*-toluidine). (*p*-toluylenediamine).

(4) 

(aniline hydrochloride). or



(Safranine).

(See p. 160.)

35. *Induline* (spirit soluble).

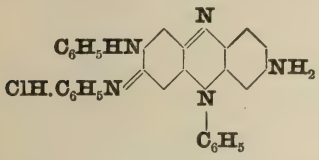
125 grams aniline.
30 „ aniline hydrochloride.

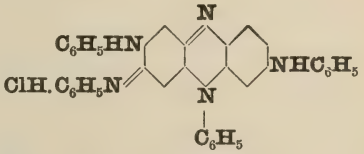
One hundred and twenty-five grams of aniline are mixed with 12 grams of concentrated hydrochloric acid in a round flask, and a solution of 7·2 grams of sodium nitrite in a little water added. The mixture is allowed to stand overnight, and is then warmed to 40–50° in order to complete the conversion of the diazoamidobenzene into amidoazobenzene.

Thirty grams of aniline hydrochloride are now added, and the mixture heated in an oil-bath, the temperature being gradually raised to 175–180° and kept at this point for four hours. The melt is poured into water and acidified with hydrochloric acid. The Induline is filtered from the solution of aniline hydrochloride, dried at 70°, and ground.

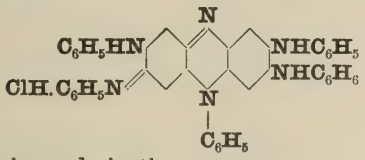
Properties.—Bluish-black powder, insoluble in water, soluble in alcohol with blue-violet colour. Dyes blue when dissolved in acetin (prepared from acetic acid and glycerine), etc., and printed on cotton.

This Induline is a mixture of the following bases :—



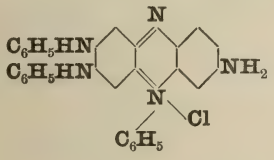


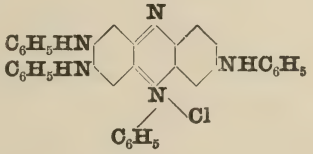
and



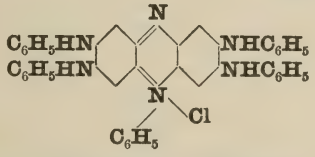
?

or formulated as *ortho*quinone derivatives





and



An explanation of their mode of formation is given on p. 164.

36. *Induline* (water soluble).

50 grams induline (spirit soluble).
300 „ conc. sulphuric acid (167 c.c.).

Fifty grams of Induline are dissolved in 300 grams of concentrated sulphuric acid and the mixture heated on the water-bath till a sample is soluble in dilute alkali.

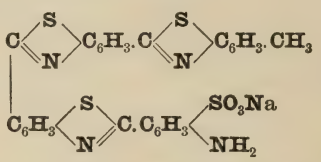
The mixture is poured into water, the sulphonated dye filtered, washed, and transferred to a porcelain evaporating basin and neutralised with caustic soda solution. The solution of the sodium salt is now evaporated down to dryness and powdered.

Properties.—Bronzy or blue-black powder, soluble in water with bluish-violet colour. Dyes wool and silk blue from an acid bath.

This substance is a mixture of the sodium salts of the sulphonic acid of the various spirit-soluble Indulines (see previous preparation).

37. *Primuline.*

Chief constituent:—



Green, *J.C.S.*, 1889, lv. 227; *Ber.*, 1889, xxii. 968.
E.P. 6319[88]; D.P. 50,525[88].

20 grams *p*-toluidine.
14 ,, sulphur.

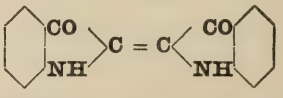
The substances are well mixed together and heated in a jar in an oil-bath. The temperature is slowly raised to 250°, sulphuretted hydrogen is evolved, and the mass becomes yellow. The reaction is finished when no more gas is evolved.

The cold mass is powdered finely, added to four times its weight of fuming sulphuric acid (30 per cent. SO_3), and warmed to 70–80° for a few minutes, till a sample dissolves in dilute alkali.

The sulphonation mixture is then poured into ten times its volume of ice-water, and the sulphonic acid of the primuline base which is precipitated is filtered and washed till free from acid. The paste is stirred up with dilute ammonia until alkaline, filtered at the pump, and washed twice with cold water. The residue is the ammonium salt of dehydrothio-*p*-toluidine sulphonic acid, which is always present, and the filtrate contains the primuline. This is saturated with salt, when the primuline separates out, and is filtered and dried.

Properties.—Yellow powder, easily soluble in water. Dyes unmordanted cotton primrose yellow from an alkaline or neutral bath; this is usually diazotised on the fibre and developed with β-naphthol, when a fast red is obtained. See also p. 172.

38. *Indigo.*



Möhlau and Bucherer, *Farbenchemisches Praktikum*, 1908, p. 288; F. Michel, *Chem. Zeit.*, 1911, xxxv. 755; H. Levinstein, *J. Soc. Dyers*, 1901, xvii., No. 6.

I. Preparation of phthalic anhydride.—

100 grams naphthalene.
1500 ,, sulphuric acid monohydrate (100 per cent.).
50 ,, mercuric sulphate.

The naphthalene is mixed with the sulphuric acid and mercuric sulphate and is dissolved by warming. The solution is now heated in a distilling flask over a sand-bath; the oxidation begins at about 200°, and the temperature is raised to 300° and the mixture heated at that point until it becomes viscid or even dry. The phthalic anhydride, which separates on cooling the distillate, is filtered off and dried.

II. Preparation of phthalimide.—

50 grams phthalic anhydride.
60 „ ammonium carbonate.

The phthalic anhydride and ammonium carbonate are placed in a round-bottomed flask, which is heated in an oil-bath to 225°. At 100° water and carbon dioxide are evolved; the mass then melts, and finally solidifies. It is dissolved in boiling water and the solution filtered. Phthalimide crystallises from the filtrate when cold.

III. Preparation of anthranilic acid.—

30 grams phthalimide.
60 „ caustic soda.
300 „ sodium hypochlorite solution (5·06 per cent.).

Thirty grams of finely powdered phthalimide are dissolved, together with 60 grams of caustic soda, in 210 c.c. of water, the solution being cooled. The latter is stirred, 300 grams of a 5·06 per cent. sodium hypochlorite solution are added, and the mixture warmed for a few minutes to about 80°, at which temperature the reaction is soon completed. After cooling, the liquid is neutralised with hydrochloric or sulphuric acid, and then acetic acid is added to precipitate the anthranilic acid, which is filtered off and washed with cold water.

IV. Preparation of ω-cyanomethylanthranilic acid. — Fourteen grams of anthranilic acid are suspended in 50 c.c. of benzene. Seven grams of finely powdered potassium cyanide are added, and, after shaking, 7·5 c.c. of a 40 per cent. solution of formaldehyde. The temperature rises considerably, and the potassium salt of ω-cyanomethylanthranilic acid is formed in the aqueous liquid.

V. Phenylglycine-o-carboxylic acid.—The benzene is removed from the above, and 20 c.c. of a 40 per cent. solution of caustic soda are added to the aqueous liquid. The mixture is heated cautiously over a wire-gauze until ammonia begins to be evolved. After the reaction has subsided the mixture is again heated until nearly all odour of ammonia has disappeared, water being added if necessary to prevent the contents of the flask becoming solid. The solution, when cold, is carefully neutralised with concentrated hydrochloric acid (using phenolphthalein paper as indicator), and then acidified with about 15 c.c. of glacial acetic acid. The yellowish-white precipitate of phenylglycine-*o*-carboxylic acid is filtered off, washed with water, and dried on a porous plate.

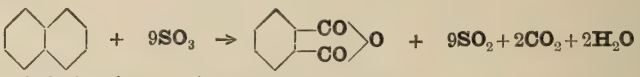
VI. Fusion of phenylglycine-o-carboxylic acid to Indigo blue.—Ten parts of phenylglycine-*o*-carboxylic acid (or the corresponding amount of the sodium or potassium salt) are added to a solution of 10–12 parts of pure caustic soda in 4–6 parts of water, and the mixture is evaporated quickly on a water bath; the mass is stirred continuously until it becomes dry. It is powdered finely and added to 8–14 parts of solid paraffin (M.-P. about 160°). The mixture is heated to 250–270°, and stirred with the thermometer. Steam is evolved and the mass

foams. The end of the reaction is indicated by the strong yellow colour of the fusion, when the temperature may be 260–280°. The homogeneous paste is cooled and boiled with water in the absence of air, or a little sodium hydrosulphite may be added to prevent oxidation. The liquid is filtered from the paraffin and oxidised by passing in air, when Indigo is precipitated.

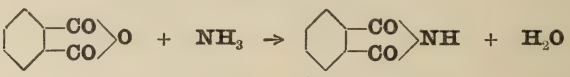
Properties.—Dark blue powder.

(For analysis, see p. 339.)

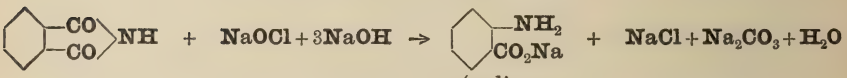
Equations.—



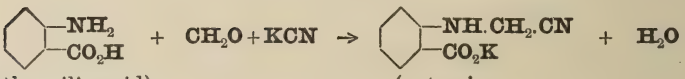
(naphthalene). (phthalic anhydride).



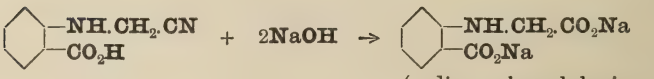
(phthalimide).



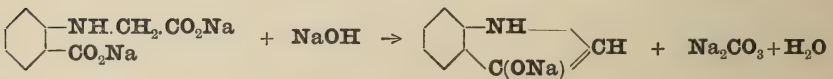
(sodium anthranilate).



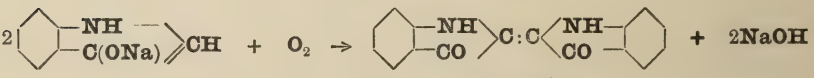
(anthranilic acid). (potassium ω-cyanomethyl-anthranilate).



(sodium phenylglycine-*o*-carboxylate).

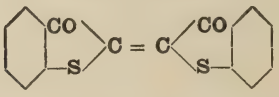


(sodium indoxyl).



(indigo).

39. *Thioindigo Red B.*



Friedländer, *Ber.*, 1906, xxxix. 1060; Möhlau and Bucherer, *Farbenchemisches Praktikum*, 1908, p. 295.

I. Preparation of Dithiosalicylic acid.—

137 grams anthranilic acid (see Indigo preparation, p. 295).
9·5 „ chloroacetic acid.
240 „ conc. hydrochloric acid (sp. gr. 1·19).
69 „ sodium nitrite (pure).
33·6 „ sulphur.
260 „ sodium sulphide (cryst.).
120 „ aqueous caustic soda (sp. gr. 1·38).
Ice.

Anthranilic acid (137 grams: 1 mol.) is mixed with 500 c.c. of water and 240 grams of concentrated hydrochloric acid, and the mixture diazotised by the addition of a concentrated aqueous solution of 69 grams sodium nitrite (1 mol.), ice being added and the usual conditions followed. The diazo solution is then slowly run, with constant stirring, into a solution containing 33·6 grams of sulphur and 260 grams of sodium sulphide in 290 c.c. of water, to which 120 grams of aqueous caustic soda (sp. gr. 1·38) has been previously added, the whole being cooled by the addition of 300 grams of ice. It is necessary to regulate the temperature throughout the addition of the nitrite solution so that it does not rise above +5°. After a short time nitrogen is evolved in large quantities, and the temperature rises to 15–25°, due to the formation of dithiosalicylic acid. After two hours, hydrochloric acid is added until the solution is acid to Congo paper, and the precipitated dithiosalicylic acid is filtered and washed with 1 litre of water.

II. Preparation of Thiosalicylic acid.—

60 grams anhydrous sodium carbonate.
100 „ iron powder.
120 „ aqueous caustic soda (sp. gr. 1·38).

The filtered and washed dithiosalicylic acid obtained in the first experiment is brought into solution as sodium salt by boiling it with an aqueous solution containing 60 grams of anhydrous sodium carbonate, the solution being filtered from any undissolved sulphur. The aqueous sodium salt is then mixed with the iron powder and the solution boiled for some hours, until a test portion on being treated with aqueous caustic alkali and filtered yields a filtrate which does not smell of hydrogen sulphide when acidified. When this stage has been reached the iron is precipitated by the addition of 120 grams of aqueous caustic soda (sp. gr. 1·38), the mixture boiled and filtered. The addition of acid to the filtrate causes the separation of thiosalicylic acid as a colourless or pale-yellow crystalline precipitate, which is filtered and washed.

III. Preparation of the o-carboxylic acid of Phenylthioglycollic acid.—

15·4 grams thiosalicylic acid.
24 „ aqueous caustic soda (sp. gr. 1·38).
9·5 „ chloroacetic acid.

The thiosalicylic acid is dissolved in the aqueous soda and is mixed with the chloroacetic acid dissolved in sufficient aqueous carbonate to form the sodium salt, the mixed solutions being gently warmed. Addition of acid precipitates the *o*-carboxylic acid, which is filtered, washed, and dried.

IV. Preparation of Oxythionaphthen (Thioindoxyl).—

20 grams *o*-carboxyphenylthioglycollic acid.
100 „ solid caustic soda.

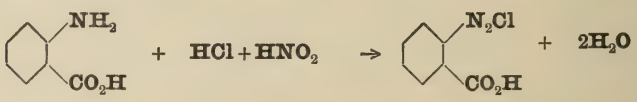
The *o*-carboxylic acid is mixed with a little water and added gradually to the 100 grams of caustic soda and 20 c.c. of water at 100°. The temperature is then raised to 170–200°, and kept at this point for one hour. Water is then added, the solution acidified, and the whole warmed until the evolution of carbon dioxide has ceased. The oxythionaphthen which separates on cooling is filtered and dried on a porous plate.

V. Preparation of Thioindigo.—

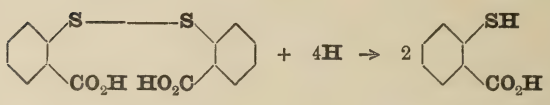
Potassium ferricyanide.

Oxythionaphthen is dissolved in sufficient dilute (5 per cent.) aqueous caustic alkali and an aqueous solution of potassium ferricyanide added until a red precipitate is no longer formed. The precipitate is then filtered, washed with water, and either dried on a porous plate or made up into paste form for future use.

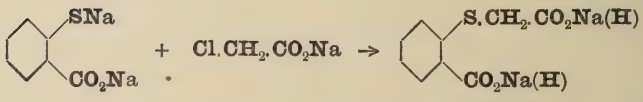
Equations.—

(1) 

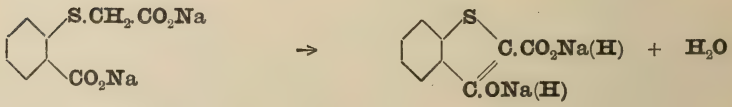
(Dithiosalicylic acid).

(2) 

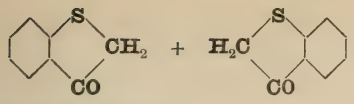
(Thiosalicylic acid).

(3) 

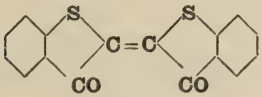
(*o*-carboxyphenylthioglycollic acid).

(4) 

(oxythionaphthen).

(5)  + 2O

(oxythionaphthen)
(keto form).

 + $2H_2O$.

(Thioindigo).

40. *Sulphur black T* (constitution unknown).

E.P. 1151[1900]; A.P. 655,659; D.P. 127,835; F.P. 299,721.

60 grams α-dinitrophenol.
90 „ sulphur (flour).
250 „ sodium sulphide (cryst.).

The sodium sulphide is dissolved in 300 c.c. of water in a round flask, the sulphur mixed with the solution, and then the dinitrophenol added gradually. The flask is attached to a reflux condenser, and heated to boiling on a sand-bath for about fifteen hours. The liquid is now transferred to a filter-flask fitted with a cork and a straight glass tube reaching to the bottom, and the side-tube connected with the vacuum pump. In this way a stream of air is led through the liquid and the dye is precipitated. When a drop on filter-paper shows a colourless rim, the mixture is filtered at the pump, dried, and powdered. Yield about 120 grams.

Properties.—Black powder, soluble in dilute solution of sodium sulphide with black colour; insoluble in alcohol. Dissolves in concentrated sulphuric acid on warming with dirty green-blue colour. Dyes unmordanted cotton in a bath containing sodium sulphide direct black.

Equation.—Unknown (see p. 195).

PART III.—ANALYTICAL.

CHAPTER XXX.

COMPOUNDS USED IN CONNECTION WITH THE DYESTUFFS.

I. INORGANIC PRODUCTS.

Fuming Sulphuric Acid.

Fuming sulphuric acid is usually looked upon for analytical purposes as a mixture of sulphur trioxide (SO_3) and sulphuric acid (H_2SO_4). It always contains, however, small quantities of sulphur dioxide (SO_2), and the amount of this is specially determined.

The fuming acid is melted, if necessary, and a sample transferred to a narrow-mouthed stoppered bottle. In order to weigh out a portion for analysis, the following method is adopted:—An ordinary test-tube, about $\frac{3}{4}$ of an inch wide, is drawn out about $1\frac{1}{2}$ inches from the bottom to a fine capillary tube about $1\frac{1}{2}$–2 inches long, which is weighed, and then the end of the capillary tube dipped into the acid. The bulb is now warmed by a flame expelling some of the air, so that, on cooling, the acid rises into it. The weight of the acid should be about 8–10 grams. The capillary end is quickly withdrawn, sealed in the flame, the tube cleaned and weighed. It is now dropped into a litre flask containing 200–300 c.c. of water, the stopper replaced, and the bulb broken by shaking. The flask is cooled for a minute under the tap, and after a short time the white fumes are entirely absorbed. The solution is poured off from the broken glass, made up to 1 litre, and 250 c.c. titrated with normal caustic soda solution, using methyl orange as indicator. It is necessary to remember here that 1 c.c. normal caustic soda solution (0·040 gram NaOH) neutralises $\frac{1}{2}$ molecule SO_3 (0·040 gram SO_2) and a whole molecule of SO_2 (0·064 gram SO_2).

A second quantity of 250 c.c. is now titrated with one-tenth-normal iodine solution (a few drops of starch solution are added, and the iodine run in till a faint blue colour is obtained).

One c.c. one-tenth-normal iodine solution corresponds to 0·0032 gram SO_2; thus for each c.c. of iodine used, 0·05 c.c. must be subtracted from the number of c.c. of normal caustic soda used in the first titration, in order to arrive at the correct amount of SO_3 present. An example will show how the calculation is made:—9·7104 grams fuming acid dissolved in water up to 1 litre, 250 c.c. taken for each analysis.

For the SO_2 determination 1·21 c.c. of one-tenth-normal iodine were used, corresponding to $1{\cdot}21 \times 0{\cdot}0032 = 0{\cdot}003872$ gram $SO_2 = 0{\cdot}16$ per cent. SO_2.

Further, by titration with methyl orange 52·38 c.c. of normal caustic soda

were used, from which 0·06 (corresponding to 1·21 c.c. of the iodine solution) are subtracted, so that we have 52·32 c.c. = 2·0928 grams SO_3 = 86·2 per cent. The fuming acid thus contains

$$86{\cdot}2\ SO_3 \qquad 0{\cdot}16\ SO_2 \qquad 13{\cdot}64\ H_2O$$

13·64 water combine with $13{\cdot}64 \times 4{\cdot}44 = 60{\cdot}56$ SO_3, so that the acid contains $86{\cdot}2 - 60{\cdot}56 = 25{\cdot}64$ per cent. SO_3.

The complete analysis is therefore

H_2SO_4	74·2
SO_3	25·64
SO_2	·16
	100·00

Zinc Dust.

Method of Knecht and Rawson.—The zinc dust is treated with excess of potassium bichromate solution in presence of sulphuric acid, whereby a portion of the bichromate is reduced.

$$3Zn + 7H_2SO_4 + K_2Cr_2O_7 = Cr_2(SO_4)_3 + 3ZnSO_4 + K_2SO_4 + 7H_2O$$

An excess of ferrous ammonium sulphate is now added, a part of which is oxidised by the bichromate remaining.

$$6(FeSO_4.(NH_4)_2SO_4.6H_2O) + K_2Cr_2O_7 + 8H_2SO_4 = 3Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 2KHSO_4 + Cr_2(SO_4)_3 + 43H_2O$$

The excess of ferrous ammonium sulphate is finally determined by titrating back with the solution of bichromate.

0·662 gram zinc dust is mixed with 80 c.c. of a solution of 25 grams $K_2Cr_2O_7$ in a litre and 10 c.c. of dilute sulphuric acid ; after ten to fifteen minutes 10 c.c. of dilute sulphuric acid is added, and after another ten minutes the same quantity of acid added. The mixture is shaken from time to time, and finally 20 c.c. of concentrated sulphuric acid and excess (about 10 grams) of pure ferrous ammonium sulphate added. After stirring the mixture, a drop withdrawn with a glass rod must give a blue colour with a drop of potassium ferricyanide solution, otherwise a further weighed quantity of ferrous ammonium sulphate must be added. The excess of the latter salt is now titrated back with the bichromate solution. The weight of bichromate reduced by the above quantity of zinc dust multiplied by 100 gives the percentage of metallic zinc.

Example.—0·662 gram zinc dust,
80 c.c. bichromate solution (25 : 1000),
10 grams ferrous ammonium sulphate,

bichromate used for titrating = 6·1 c.c. (1 gram ferrous ammonium sulphate = 0·1253 gram $K_2Cr_2O_7$), total bichromate solution used = 86·1 c.c. = 2·1525 $K_2Cr_2O_7$, bichromate used by ferrous ammonium sulphate = $0{\cdot}1253 \times 10$ = 1·253 ; therefore $2{\cdot}1525 - 1{\cdot}253 = 0\ 8995$ gram $K_2Cr_2O_7$ is the amount reduced by the zinc, and the zinc contained in the zinc dust = 89·95 per cent.

Wahl's method.—Half a gram of zinc dust is shaken with 25 c.c. of cold water, and to the mixture 7 grams of pure neutral ferric sulphate are added. After about a quarter of an hour the zinc will have dissolved, leaving the impurities suspended in the liquid, an equivalent amount of the ferric sulphate having been reduced. The solution is now acidified and titrated with potassium permanganate solution.

Lead Peroxide.

About 10 grams of paste are weighed out and washed into a litre flask. 100 c.c. of a half-normal oxalic acid solution and 150 c.c. of dilute sulphuric acid (1 : 3) are then added and the mixture shaken for one hour. The flask is now filled up to the mark, the contents filtered, and 250 c.c. measured into a basin. Distilled water and 50 c.c. of dilute sulphuric acid are added, and the excess of oxalic acid titrated back with standard permanganate solution. 1 gram crystallised oxalic acid = 1·8968 grams PbO_2.

Sodium Sulphide.

The technical product may be rapidly tested by the volumetric method described by Battegay (*Zeit. Farb. Ind.*, 1903, 350).

The solution of sodium sulphide to be analysed is treated carefully with dilute acetic acid in presence of phenolphthaleïn, till the latter is colourless, so as to neutralise any free alkali which may be present.

A standard solution of crystallised zinc sulphate is now run in from a burette till all the soluble sodium sulphide is converted into the insoluble zinc sulphide. In order to indicate the presence of still unchanged sodium sulphide, cadmium sulphate is used. A concentrated solution of the latter is prepared and spotted on thick white blotting-paper (not ordinary filter-paper). A drop of the liquid being analysed is brought into contact with the cadmium sulphate, and as long as any soluble sulphide is present a yellow stain of cadmium sulphide will be formed. With a little practice the end point is easily found.

Example.—5·2015 grams of sodium sulphide dissolved in water up to 250 c.c. 25 c.c. required; 9·4 c.c. two-fifths-normal zinc sulphate (57·514 grams $ZnSO_4.7H_2O$ in 1 litre).

$$Na_2S \text{ in } 25 \text{ c.c.} = \frac{9{\cdot}4 \times 0{\cdot}078}{5} = 0{\cdot}1466 \text{ gram; percentage of } Na_2S = \frac{10 \times 0{\cdot}1466 \times 100}{5{\cdot}2015} = 28{\cdot}16.$$

Podreschetnikoff's method (*Zeit. Farb. Ind.*, 1907, 388), is as follows:— 9·052 grams of the sample are dissolved in 500 c.c. of air-free distilled water; 10 c.c. of this solution are diluted with 150 c.c. of water and titrated with decinormal sulphuric acid, using phenolphthaleïn as indicator (requiring, say, 12·8 c.c.). An excess (about 10 c.c.) of neutral formaldehyde solution is now added, and decinormal acid run in until the solution again becomes colourless, the amount of acid required being, say, 12·5 c.c. The calculation is then as follows:

In 100 c.c. the free $NaOH$ = 12·8 − 12·5 c.c. = 0·3 c.c. $N/10$ solution = 0·0012 gram = 0·66 per cent.

$NaOH$ from Na_2S = 12·5 c.c. $N/10$ solution = 0·05 gram.
$NaOH$,, $NaSH$ = 12·5 c.c. ,, ,, = 0·05 ,,

The two latter quantities correspond with 53·85 per cent. Na_2S.

Sodium Nitrite.

Sodium nitrite is analysed by the permanganate method in acid solution.

$$2KMnO_4 + 5NaNO_2 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 5NaNO_3 + 3H_2O$$

The sodium nitrite solution is run from a burette into a certain quantity of permanganate solution strongly acidified with dilute sulphuric acid, which is

warmed to 40–50°. The end of the reaction is shown by the disappearance of the pink colour. For example :—20 c.c. of a half-normal (or 100 c.c. of one-tenth-normal) solution of potassium permanganate are acidified with dilute sulphuric acid, warmed to the above temperature, and a solution of 1 gram of sodium nitrite in 100 c.c. of water added from a burette till the colour disappears. One c.c. half-normal permanganate (16 grams per litre) corresponds to 0·01725 gram sodium nitrite; therefore 20 c.c. permanganate = 0·345 gram $NaNO_2$, and if n c.c. of the nitrite solution have been used, the percentage of $NaNO_2 = \frac{3450}{n}$. Technical sodium nitrite is 97 to 98 per cent. $NaNO_2$ (see also Lunge-Keane, *Technical Methods of Chemical Analysis*, 1911, Vol. II. Part ii., p. 927).

Sodium Hyposulphite.

Sodium hyposulphite (technically and incorrectly known as "hydrosulphite"), which is so much used in the preparation of the "hydrosulphite vat," is best estimated by Knecht and Hibbert's method (*Ber.*, 1907, xl. 3819) :—A weighed quantity (about 0·2 gram) is added to 25 c.c. of a solution of methylene blue containing 10 grams of the dyestuff per litre. The methylene blue solution is contained in a conical flask, through which a slow current of carbon dioxide is passed. On dissolving in the methylene blue solution, the hyposulphite reduces its equivalent of the dyestuff, and the excess is estimated, after adding acetic acid, by titration with standard titanous chloride (see p. 336). The presence of bisulphites or sulphites in the hyposulphite does not interfere with the analysis.

II. ORGANIC PRODUCTS.

Aliphatic Compounds.

Formaldehyde.

The commercial solution of formaldehyde in water contains about 40 per cent. CH_2O.

The sample for analysis is shaken with precipitated chalk, allowed to stand, and 5 c.c. of the clear solution are added to 50 c.c. normal ammonia solution in a flask which is stoppered and allowed to stand for one day. The excess of ammonia is now titrated back with normal hydrochloric acid, using litmus as indicator.

From the equation

$$6CH_2O + 4NH_3 = \underset{\text{hexamethylene-tetramine,}}{C_6H_{12}N_4} + 6H_2O$$

the above quantity of ammonia would combine with 2·4 grams formaldehyde, corresponding to a 48 per cent. solution. For each c.c. of hydrochloric acid used in titrating the excess of ammonia, 0·048 gram of formaldehyde is subtracted from this amount.

If n c.c. of normal acid have been used, the percentage of formaldehyde $= 48 - n \times 0{\cdot}96$ (Legler, *Ber.*, xvi. 1333).

For a very exact method see Blank and Finkenbeiner (*Ber.*, 1898, xxxi. 2979).

Formaldehyde is used for the preparation of Auramine, triphenylmethane colours, and certain colours of the acridine series.

Methyl Alcohol.

Methyl alcohol is used in the colour industry for the preparation of dimethylaniline, formaldehyde, and methyl chloride, bromide, and iodide. The chief impurity to be met with is acetone, which is tested for by Krämer's method (*Ber.*, xiii. 1002). Into a stoppered measuring cylinder of 50 c.c. capacity, 10 c.c. of caustic soda solution (80 grams NaOH in 1 litre) are measured, then 1 c.c. of the methyl alcohol, and lastly, after shaking, 5 c.c. of iodine solution (containing 254 grams iodine in 1 litre). After standing for some time 10 c.c. of alcohol-free ether are added and the cylinder shaken. The volume of the ethereal solution is now read off, an aliquot part (about 5 c.c.) withdrawn with a pipette, transferred to a weighed watch-glass, and the ether allowed to evaporate, when the iodoform separates out as yellow crystals. The watch-glass is left in a desiccator, containing sulphuric acid, for some time and then weighed. One molecule acetone, $C_3H_6O = 58$, gives 1 molecule iodoform, $CHI_3 = 394$. From the determination of the specific gravity (which is always made) the weight of 1 c.c. of methyl alcohol is given, and the amount of acetone contained in it easily calculated.

Methyl alcohol boils at 66–67°, and has a specific gravity of 0·79647 at 15° compared with water at the same temperature.

Formic Acid.

Formic acid is estimated by oxidation with potassium permanganate. A measured volume of formic acid solution, containing not more than 1 per cent. of the acid, is placed in a stoppered flask, an excess of decinormal permanganate solution and 0·5 gram of anhydrous sodium carbonate are added, and the mixture is heated on the water-bath for half an hour. After cooling, 75 c.c. of water, 25 c.c. of dilute sulphuric acid, and 2 grams of potassium iodide are added, and the liberated iodine is titrated with thiosulphate solution. Pure anhydrous formic acid melts at 8·6°, boils at 100·6° under 760 mm. pressure, and has a specific gravity of 1·22 at 20°.

Acetic Acid.

Acetic acid is usually estimated by titration with standard caustic soda solution using phenolphthaleïn as indicator. It boils at 118°, and has a specific gravity of 1·0553 at 15°.

Aromatic Compounds.

Benzene.

"Pure benzene" should distil within one degree of the correct boiling-point (80·5°). It should give no crystalline precipitate on standing with a few drops of phenylhydrazine (carbon bisulphide). On shaking with concentrated sulphuric acid, the latter should only be slightly darkened (thiophene or hydrocarbons of the ethylene series). On shaking with sulphuric acid and a fragment of isatin, no blue colour should be produced (thiophene). On treatment with a mixture of nitric and sulphuric acids and distillation with steam, no unnitrated hydrocarbon should be obtained (hydrocarbons of the paraffin series). It should solidify on cooling below 0° (M.P. 6°).

"Crude benzene" is a mixture of benzene, toluene, and a little xylene, and is

known as "30s.," "50s.," or "90s.," according as 30 per cent., 50 per cent., or 90 per cent. of the whole (by volume) distils before a 100° is reached.

These give the following numbers on distillation :—

	30s.	50s.	90s.
To 85°	0 per cent.	0 per cent.	25 per cent.
,, 90°	2 ,,	4 ,,	70 ,,
,, 95°	12 ,,	26 ,,	83 ,,
,, 100°	30 ,,	50 ,,	90 ,,
,, 105°	42 ,,	62 ,,	94 ,,
,, 110°	70 ,,	71 ,,	97 ,,
,, 115°	82 ,,	82 ,,	98 ,,
,, 120°	90 ,,	90 ,,	99 ,,

By carefully distilling 100 c.c. of the benzene from a small distilling flask and collecting the distillate in a measuring cylinder, the quality of the product is valued by the amount which is read off when the thermometer registers 100°. (See also Frank, *J.S.C.I.*, 1901, 166.) For the estimation of sulphur in benzene, see Schwalbe, *Zeits. Farb. Ind.*, 1905, 113.

Toluene.

Commercial toluene should only be slightly darkened on shaking with concentrated sulphuric acid.

It should distil within one degree (111–112°). B.P. 111°.

Xylene.

The three isomeric xylenes occurring in coal-tar are not separated on the large scale.

The commercial product should distil within a few degrees; for example:—

To 138° . . .	10 per cent.
,, 139° . . .	70 ,, ,,
,, 140° . . .	88 ,, ,,
,, 140·5° . . .	90 ,, ,,

Naphthalene.

Commercial naphthalene is nearly chemically pure. It should melt at 79·2° and boil correctly within one degree (B.P. 218°). It must be white and volatilise without residue. By shaking with concentrated sulphuric acid it must not become dark-coloured.

Naphthalene should not contain phenols or quinoline bases. To test for phenols, 1–2 grams are boiled with 30 c.c. dilute caustic soda, the solution cooled and filtered from naphthalene. To the filtrate is added a little bromine water and hydrochloric acid. If phenols are present, a precipitate of bromo-phenols is obtained. Quinoline bases are tested for by dissolving the naphthalene in concentrated sulphuric acid, pouring the solution into water, and after filtering from naphthalene and making the filtrate alkaline, distilling in steam. Quinoline bases distil over and are recognised by their smell.

Nitrobenzene.

Pure nitrobenzene boils at 205° and has a specific gravity of 1·209 at 15°. It should distil almost completely within 1°.

Nitrotoluene.

1. Orthonitrotoluene should boil from 222–225°.
2. Paranitrotoluene should melt at 54°.

The ortho-compound is used for the preparation of *o*-toluidine and of tolidine. The para-compound is used for the preparation of *p*-toluidine and of certain dyes.

m-*Dinitrobenzene.*

The commercial product should be light in colour and not contain oil (nitrobenzene). It should have nearly the right melting-point (89·8°), should be neutral, and give a clear solution in alcohol.

m-*Dinitrotoluene*

should not be oily, and should melt nearly correctly (M.P. 70·5°).

Aniline.

1. "Aniline for blue."—The aniline to be used for the manufacture of Aniline blue (triphenylrosaniline) must be as pure as possible, and consequently is known by this name. The commercial product should be nearly chemically pure.

The sp. gr. varies between 1·0265 and 1·0267 at 15°. A good sample should nearly all distil (97 to 98 per cent.) within 1–1½°. The boiling-point is 182°. 10 c.c. of the oil should give a clear solution with a mixture of 50 c.c. of water and 40 c.c. hydrochloric acid.

The following table shows the behaviour of various samples of Aniline for blue on distillation :—

Specific Gravity at 15°.	1. 1·0260.	2. 1·0252.	3. 1·0256	4. 1·0260.	5. 1·0260.
Percentage volume distilling over up to 180°	1	2	2	3	1
,, ,, ,, 181°	2	4	4	4	4
,, ,, ,, 182°	93	83	89	88	92
,, ,, ,, 183°	2	7	2	2	2
,, ,, ,, 184°	...	2	...	...	...
Total, . .	98	98	97	97	99

Estimation of water in aniline oil (Liebmann and Studer, *J.S.C.I.*, 1889, xviii. 110).—100 c.c. of the sample are distilled and 10 c.c. collected in a narrow graduated measure holding 15 c.c.; 1 c.c. of saturated salt solution is added, the whole is well shaken, and left to settle. The increase in volume of the brine + a correction of 0·3 c.c. gives the amount of water.

The boiling is now continued, and the temperature is observed in intervals of 10 c.c.; 80 per cent. of the oil should boil within 0·5°.

Specific gravity.—This should be taken with the distillate after the water has been removed; good oils have a sp. gr. from 1·0265–1·0270 at 15°.

Sulphur compounds.—These are given off as hydrogen sulphide on boiling. The sample is boiled for some hours in a reflux apparatus, while a current of carbon dioxide is passed through, carrying the evolved hydrogen sulphide into a measured quantity of one-tenth-normal silver nitrate; at the end of the operation the silver sulphide is removed, and the silver remaining in the solution estimated; from the loss the amount of sulphur is calculated.

"Aniline salt" (aniline hydrochloride).—Moisture is determined by drying 5 grams for twenty-four hours in a desiccator. The loss should not be more than 1 per cent. The melting-point should be correct (192°).

Free acid is determined as follows:—5 grams of the salt are dissolved in 10 c.c. of water, and 5 drops of crystal violet (1 : 1000) added, and the mixture compared with a similarly made solution of aniline salt free from acid. If, now, the sample shows acidity—namely, a bluer or even a green shade—a decinormal aqueous solution of aniline is run in until the colours are exactly alike, and the amount of free acid is readily found by calculation.

The aniline is estimated by Reinhardt's method (see below); for this determination the dried salt is used. The formula to be used is

$$X = 2{\cdot}5102VT - 1{\cdot}1502A,$$

where A = the weight of aniline salt taken,

X = the quantity of real aniline hydrochloride,

T = the titre of the bromine solution for aniline hydrochloride, obtained from the aniline titre by multiplying by $\frac{129{\cdot}5}{93}$, and V the number of c.c. of bromide solution used.

2. "Aniline for red."—This is a mixture of aniline with ortho- and para-toluidine, and is used for the manufacture of Magenta.

Red oil should have a sp. gr. of 1·006–1·009 at 15°. It should distil completely between 182° and 198°, and should dissolve clearly in dilute hydrochloric acid.

The following table shows the quantities obtained by the distillation of two samples of red oil:—

Specific Gravity at 15°.	I. 1·009.	II. 1·008.
Percentage volume distilling over up to 189°	27	19
,, ,, ,, 191°	39	38
,, ,, ,, 193°	17	22
,, ,, ,, 195°	7	6
,, ,, ,, 197°	5	6
,, ,, ,, 198°	2	3
Total, . .	97	97

Reinhardt's method for the analysis of aniline oils (*Chem. Zeit.*, 1893, 413).—The method depends on the fact that:—

1. By treatment with a mixture of potassium bromide and bromate in dilute acid solution, aniline gives tribromoaniline; *o*- and *p*-toluidine yield *di*-substitution products.

(2) Under certain conditions, if oxalic acid be added to the hydrochloric acid solution, *p*-toluidine first, then aniline, is precipitated, while *o*-toluidine remains in solution.

The precipitated oxalates are converted into the corresponding oils, and the relation of aniline to *p*-toluidine determined by titration with the bromine solution.

I. Determination of aniline, o- *and* p-*toluidine, and aniline in mixtures with* o- *or* p-*toluidine or both toluidines.*—The "bromine" solution is prepared by boiling a mixture of 480 grams of bromine, 336 grams potassium hydroxide (100 per cent.), and 1 litre of water for two to three hours. The solution is diluted to 9 litres.

For standardising this solution, as well as for analysis, 1·5–2 grams of oil are dissolved in 100 c.c. of hydrobromic acid of sp. gr. 1·45–1·48 (or the corresponding quantity of potassium bromide and hydrochloric acid) and 1000 c.c. of distilled water, and the "bromine" solution added till starch-iodide paper shows a blue colour (presence of bromine). The titre of the solution is obtained with pure aniline.

The amount of aniline in technical aniline oil is given by the formula

$$x = 2{\cdot}3777vt - 1{\cdot}377a \text{ and percentage} = \frac{x{\cdot}100}{a}$$

where x is the quantity of aniline in the quantity a of oil taken, v the c.c. of bromine solution used, and t the aniline titre of the latter (weight of aniline in 1 c.c.). $a - x$ is the quantity of toluidine in the oil.

II. Determination of p-*toluidine in mixtures with aniline or* o-*toluidine or both bases.*—In order to obtain exact results more oxalic acid must be used than corresponds to the *p*-toluidine present in the oil. This must, therefore, be roughly determined by a preliminary experiment.

If 100 grams are taken for analysis, the amount of *p*-toluidine found in the preliminary experiment is increased by 10 grams in the case of oils containing little aniline, and 20 grams when more aniline is present, for the purpose of calculating the amount of oxalic acid to be used.

The analysis is carried out in the following manner:—100 grams of oil are mixed with 106 grams of hydrochloric acid (free from sulphuric) of 31 per cent. HCl (or a corresponding amount). This mixture is at once treated with the boiling solution of oxalic acid in ten times its weight of distilled water. The solution must be quite clear when just prepared. It is now allowed to cool and left for forty-eight hours, when the oxalates of *p*-toluidine ($C_7H_9N.C_2H_2O_4$) and aniline have crystallised out, and are filtered, washed with 25 c.c. of distilled water three times, and decomposed by adding to a hot dilute solution of caustic potash (45 grams KOH, 250 c.c. distilled water). After cooling, the oil is separated and weighed. It is then dried with quicklime, and the amount of aniline determined as above by titration with bromine solution. A simple calculation gives the amount of *p*-toluidine in the original oil, to which a correction of + 2·00 must be added.

A modification of Reinhardt's process is given by Schaposchnikoff and Sachnowsky (*J. Russ. Chem. Soc.*, 1903, xxxv. 72; also *J.C.S.*, 1903, xxxiv. 395, and *Zeit. Farb. Ind.*, 1903, 7), which depends on the bromination of the two amines (aniline and toluidine) by potassium bromate in hydrobromic acid solution. The potassium bromate used is the recrystallised commercial product, of which an 8 per cent. solution is prepared, the strength being determined by mixing 25 c.c. with 5 grams of potassium iodide and 3 c.c. of 25 per cent.

hydrobromic acid solution, and estimating, by titration with standard thiosulphate, the iodine set free according to the equation $KBrO_3 + 6HBr + 6KI = 3I_2 + 7KBr + 3H_2O$. 1 gram of iodine corresponds with 0·22083 gram of potassium bromate, that is, with 0·12231 gram of aniline, or 0·14061 gram of toluidine.

About 1 gram of the aniline oil is dissolved in about 60 grams of 25 per cent. hydrobromic acid solution, and the bromate solution run in until the clear liquid above the bromide precipitate assumes a yellow coloration. Then, if a is the weight of oil taken, n the number of c.c. of bromate solution employed, t_a and t_t the amounts of aniline and toluidine respectively corresponding with 1 c.c. of the bromate solution, the percentage of aniline in the oil is given by $\frac{100t_a(nt_t - a)}{a(t_t - t_a)}$, and that of the toluidine by $\frac{100t_t(a - nt_a)}{a(t_t - t_a)}$.

Dimethylaniline.

B.P. 192°; sp. gr. 0·9553 at 15°.

The commercial product is usually nearly pure. The chief impurity is monomethylaniline.

This is estimated by mixing 5 c.c. of the oil with 5 c.c. of acetic anhydride and observing the rise of temperature; each degree rise indicates about ½ per cent. of monomethylaniline.

The oil should have the correct specific gravity, and distil between 190° and 192°.

The presence of aniline in the oil is detected by adding a drop or two of concentrated sulphuric acid to the ethereal solution. If aniline be present, a precipitate of aniline sulphate will be formed.

Diethylaniline.

B.P. 213·5°; sp. gr. 0·939 at 18°.

The amount of monoethylaniline is estimated as under dimethylaniline by mixing with acetic anhydride.

The oil should distil to the extent of 90 per cent. between 212° and 214°.

Naphthylamine.

I. *α-Naphthylamine*, M.P. 50°.—The commercial product should have nearly the right melting-point, and should give a clear solution with warm dilute hydrochloric acid.

II. *β-Naphthylamine*, M.P. 112°, should not smell of α-naphthylamine, should have nearly the correct melting-point, and should dissolve nearly completely in dilute hydrochloric acid.

Other derivatives which come on the market are Naphthylamine S, which is α-naphthylamine sulphate; Developer B, ethyl-β-naphthylamine.

Nitranilines.

The nitranilines which are used technically are the meta, M.P. 115°, and para, M.P. 147°.

They are tested with half-normal nitrite solution.

For the analysis, 1·38 grams are weighed out and dissolved in water with addition of 7 c.c. concentrated hydrochloric acid.

Detection of m-*nitraniline in* p-*nitraniline* (Liebmann, *J.S.C.I.*, xvi. 294).—0·25 gram of *p*-nitraniline is heated with hydrochloric acid and zinc dust in a flask fitted with a bunsen valve till the solution is colourless. The mixture is filtered and diluted to 250 c.c. If 10 c.c. of this solution is diluted to 50 c.c., and one to two drops of a dilute solution of sodium nitrite added, a pale-yellow coloration is produced. If, however, the substance contained *m*-nitraniline, the solution becomes brown, due to the formation of Bismarck brown.

p-Nitraniline also comes on the market in the form of its diazo-compound for the production of "para"-reds (see p. 51).

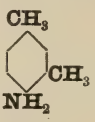
Sulphanilic Acid.

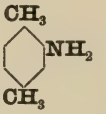
The commercial product sometimes contains a little aniline.

It is dissolved in water with addition of caustic soda; the alkaline solution boiled for some time to drive off the aniline, and, after cooling and acidifying, titrated with half-normal nitrite.

Xylidine.

Commercial xylidine is a mixture of five isomers, viz.:—

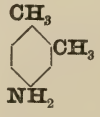
m-xylidine . . . .  about 40 per cent.

p-xylidine . . . .  „ 30 „

and small quantities of

2-amino-*m*-xylene . . .

3-amino-*o*-xylene . . .

and 4-amino-*o*-xylene . 

The oil should boil between 210° and 220° and have a sp. gr. of 0·9815–0·9840. It should give a clear solution with dilute hydrochloric acid.

The meta-compound is separated by adding glacial acetic acid, and the para-, as hydrochloride, by adding hydrochloric acid to the filtrate from the *m*-xylidine acetate.

(E.P. 6899[88]; D.P. 39,947[86]. Hodgkinson and Limpach, *J.C.S.*, 1900, lxxvii. 65.)

o-*Toluidine.*

B.P. 197°; sp. gr. 1·0037 at 15°.

The presence of aniline is detected by the production of a violet colour on shaking the ethereal solution with a solution of bleaching-powder.

For the estimation of *p*-toluidine in commercial "fluid toluidine," the method of Merz and Weith (*Ber.*, ii. 433) is used:—10 c.c. of the oil, which has been dried over solid caustic potash, is heated with 10 c.c. of acetic anhydride for two hours at 140°, the product is mixed with 30 c.c. of acetic acid and poured into 800 c.c. of cold water. After standing for two days the separated aceto-*p*-toluidide is filtered off, washed with dilute acetic acid (10 per cent.), dried, and weighed. From this weight the percentage of *p*-toluidine is calculated (100 acetyl compound = 71·8 *p*-toluidine).

When small quantities of *p*-toluidine are present (under 10 per cent.) the following colorimetric method of Schoen is used:—A standard oil is prepared containing 8 per cent. of *p*-toluidine and 92 per cent. of *o*-toluidine; 1 c.c. of which is dissolved with 2 c.c. of pure hydrochloric acid in 50 c.c. of water, and oxidised cold by adding 1 c.c. of a saturated solution of potassium bichromate. After standing for two hours the product is filtered, the precipitate being washed with water, and the filtrate and washings made up to 100 c.c. The toluidine to be tested is treated in the same manner, and compared colorimetrically with the above solution.

Commercial "pure orthotoluidine" should give under 1 per cent. of *p*-toluidine when tested as above. "Fluid toluidine" should boil within two degrees, and have a sp. gr. of 0·9995 to 1·0005. It should give a clear solution with hydrochloric acid.

m-*Phenylenediamine and* m-*Toluylenediamine.*

M.P. 63°; B.P. 287°.

Commercial *m*-phenylenediamine comes on the market either as the free base or the crystalline hydrochloride, $C_6H_4(NH_2)_2.2HCl$.

It is analysed by titration with a decinormal solution of diazobenzene (or xylene) chloride.

The diazo-solution is prepared as follows:—

9·3 grams of pure aniline (or 12·1 grams of xylidine) are washed into a beaker and dissolved by the addition of 30 c.c. concentrated hydrochloric acid. A handful of chopped ice is thrown in and water added till the volume is about 500–600 c.c. 100 c.c. of normal nitrite solution (6·9 grams $NaNO_2$) are now slowly added, and towards the end the solution is carefully tested with starch-iodide paper. When the aniline is completely diazotised only a very faint blue colour should be obtained on the paper. The cold solution is now transferred to a litre flask and made up to the mark with ice-water. The flask is kept in a basin and packed in ice. The diazo-solution should not be above 2°.

In using diazo-solutions in a burette, analyses should either be rapidly carried out, or the burette jacketed and the intervening space filled with ice-water.

For the analysis, 5·4 grams of the sample are weighed out, dissolved in water, and made up to 1 litre. 100 c.c. are withdrawn, transferred to a beaker, sodium acetate solution added, and the solution titrated with the diazo-solution.

As soon as the diazo-solution is added, the formation of the azo-colour (Chrysoïdine) will be noticed, and a little salt is added to cause the colour to be

entirely precipitated. The mixture is frequently spotted on paper; the dye should remain in the centre, leaving a colourless rim. The progress of the analysis is seen by the behaviour of the rim when a drop of diazo-solution is brought in contact with it. If an orange streak is noticed at the junction of the rim with the diazo-solution, the phenylenediamine is not all combined, and more diazo-solution is run into the beaker. This test is continually repeated, the streak becomes fainter gradually, and when no colour is seen the titration is finished. Care must be taken not to add too much diazo-solution; this is shown by testing the rim with phenylenediamine solution, when the orange colour will appear. If a reaction is obtained with both diazo-solution and phenylenediamine solution, more sodium acetate must be added to the beaker.

The number of c.c. of diazo-solution used, multiplied by 2 = the percentage of *m*-phenylenediamine in the sample.

m-Toluylenediamine, M.P. 99°, is tested in exactly the same way. 6·1 grams are weighed out.

Both these diamines are used as developers.

Nerogen D is chloro-*m*-phenylenediamine, $C_6H_3(NH_2)_2Cl = 1 : 3 : 5$. F.P. 286,888[99].

Benzidine, Tolidine, Dianisidine.

M.P.'s 127·5–128°, 129°, 137° respectively.

These bases come on the market almost chemically pure. They are tested by titration with half-normal sodium nitrite.

This solution is prepared by dissolving 36 grams of sodium nitrite in water and making the solution up to 1 litre. The solution is standardised by potassium permanganate (see p. 302).

For the analysis, 1·84 grams of benzidine, 2·12 grams of tolidine, or 2·44 grams of dianisidine are weighed out and dissolved in hot water with addition of 7 c.c. concentrated hydrochloric acid. The clear solution is cooled with ice to 5–10°, and the nitrite solution added till a reaction is obtained with starch-iodide paper, which remains five minutes.

The number of c.c. of nitrite solution used, multiplied by 2·5 = the percentage of base present.

Dianisidine also comes on the market in the form of its tetrazo-compound as Azophor blue D, which is the tetrazo-sulphate mixed with sodium hydrogen sulphate.

Developer NB is nitrobenzidine.

Phenol.

M.P. 42°; B.P. 181·5°.

The commercial product should melt at about 40°, and dissolve completely in dilute caustic soda.

Estimation of phenol (Messinger and Vortmann, *Ber.*, 1890, xxiii. 2753).—The method depends on the fact that phenol absorbs 3 atoms of iodine, *i.e.* 1 molecule of phenyl requires 3 molecules of iodine. 2–3 grams of phenol are dissolved in caustic soda; at least 3 molecules of alkali to 1 of phenol must be taken. The solution is diluted to 250 or 500 c.c.; 5 or 10 c.c. measured into a small flask, and warmed to about 60°. One-tenth-normal iodine solution is now added till the liquid is coloured yellow, and the flask shaken, when a reddish-coloured precipitate is formed. The flask is cooled, the contents acidified with dilute sulphuric acid, and diluted to 250 or 500 c.c. Of this,

100 c.c. are filtered and the excess of iodine titrated with one-tenth-normal sodium thiosulphate (using a few drops of starch solution as indicator).

The amount of iodine absorbed by the phenol, multiplied by $\frac{94{\cdot}048}{761{\cdot}1}$ or 0·123568, gives the amount of phenol.

See also Riegler, *J.C.S.*, 1900, lxxviii. 112, and Schryver, *J.S.C.I.*, 1899, xviii. 553.

Resorcinol.

M.P. 118°.

The commercial product should be light in colour, and should not become brown on exposure to air. It should have the right melting-point, and give a clear solution with water. Water is estimated by drying over sulphuric acid.

Benzaldehyde.

B.P. 180°; sp. gr. 1·053.

The technical product must be colourless, have a sp. gr. of 1·052–1·055, and distil completely between 176° and 180° in a stream of hydrogen (to prevent part oxidising to benzoic acid).

It must give a clear mixture with concentrated sulphuric acid, and dissolve in ammonium bisulphate without leaving any oily residue. To estimate the presence of benzoic acid, 50 c.c. of the sample are shaken with 10 c.c. normal caustic soda and water, using phenolphthaleïn as indicator, and the excess of caustic soda is titrated back with normal acid. 1 c.c. normal NaOH = 0·122 gram $C_6H_5.COOH$.

Benzoic Acid.

M.P. 120°.

The technical product should be colourless and volatilise without residue. It should have the right melting-point, and give a clear solution with dilute ammonia, benzene, and ether.

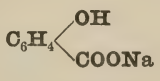
The strength is tested by titration with normal caustic soda, using litmus as indicator. On account of the slight solubility in water, it is best to add an excess of caustic soda and titrate back with one-tenth-normal acid.

Salicylic Acid.

M.P. 156°.

The technical product must be white and not smell of phenol.

The strength is estimated by titration with normal caustic soda in the same manner as in the case of benzoic acid. The end point is reached when the salt



is formed. The disodium salt has an alkaline reaction.

Phthalic Anhydride

M.P. 128°.

The technical product should form colourless needles, and have the right melting-point. It should be soluble in benzene and volatilise without leaving a residue.

The Naphthols.

α-Naphthol, M.P. 94°.—The technical product forms white crystalline lumps. The chief impurity is β-naphthol (see below).

β-Naphthol, M.P. 123°.—The commercial product should have nearly the right melting-point and dissolve almost completely in dilute caustic soda.

Detection of α-naphthol in β-naphthol. Method of Leger (*Bull. Soc. Chim.*, 1897 [iii.], xvii. 546).—A cold saturated solution of naphthol is prepared by grinding with water in a mortar and, after standing some time, filtering. On the other hand, a solution of sodium hypobromite is prepared by dissolving 5 c.c. of bromine in a solution of 12 grams of caustic soda in 130 c.c. of water. Ten c.c. of the naphthol solution are treated with a few drops of the hypobromite solution. α-Naphthol gives a dirty violet precipitate, whilst β-naphthol gives a yellow colour. In this way 1 per cent. of α-naphthol in β-naphthol may be detected. The solutions must be freshly prepared. Liebmann (*J.S.C.I.*, 1897, xvi. 294) proceeds as follows:—0·144 gram of the β-naphthol is dissolved in 5 c.c. of absolute alcohol contained in a graduated test-tube, and the solution made up to 15 c.c. with pure toluene; 0·14 gram of paranitraniline dissolved in 9 c.c. of dilute hydrochloric acid is then cooled and diazotised with 1 c.c. of normal sodium nitrite, and 1 c.c. of the diazo-solution added to the tube containing the β-naphthol. Water is then added, the toluene solution separated and shaken with 5 c.c. of normal caustic soda, and the colour of the alkaline solution compared with that of the alkaline solution obtained in exactly the same way from β-naphthol containing a known quantity of α-naphthol. The test is based on the fact that the hydroxyazo derivative obtained from α-naphthol and paranitraniline is soluble in alkalies, whereas the corresponding β-naphthol derivative is insoluble. β-Naphthol can readily be freed from α-naphthol by crystallising it from toluene, washing the crystals first with a mixture of toluene and light petroleum, then with the latter alone, steaming and crystallising the steamed product several times from boiling water.

Naphthol Sulphonic Acids.

Certain of these acids (*e.g.* Nevile and Winther acid, Schäffer salt, R salt, F acid) may be titrated with standard diazobenzene solution in alkaline solution (sodium carbonate) (see p. 311); but a more accurate method is that due to Vaubel (*Chem. Zeit.*, 1893, 1265, 1897), which depends on the fact that these acids absorb one atom of bromine.

The analysis is carried out by titrating an acidified solution of the acid, to which potassium bromide has been added, with a solution of potassium bromate of known strength, when bromine is liberated according to the equation

$$5KBr + KBrO_3 + 6H_2SO_4 = 3Br_2 + 6KHSO_4 + 3H_2O.$$

The bromine is absorbed rapidly by the naphthol sulphonic acid, and the end of the reaction is shown by starch-iodide paper becoming blue. The experiment is carried out at 30–40°.

The potassium bromate solution is made by dissolving pure recrystallised potassium bromate (11·14 grams) in water and making up to 1 litre. 1 c.c. of this solution = 0·0696 gram R salt (mol. 348) or 0·0492 gram Schäffer, F, or Nevile and Winther acid (mol. 246).

For analysis, $\frac{1}{100}$ molecule of the naphthol sulphonic acid is weighed out, dissolved in water, acidified with a few c.c. of dilute sulphuric acid, and, after adding a few crystals of potassium bromide, titrated with the solution of bromate at 40°, using starch-iodide paper as indicator.

The number of c.c. of bromate solution used, multiplied by 2, gives the percentage.

Amidonaphthol sulphonic acids are titrated with standard diazobenzene solution in presence of sodium carbonate.

Naphthylamine Sulphonic Acids.

These are tested by titration with half-normal nitrate: $\frac{1}{100}$ molecule of the acid is weighed out (*e.g.* 2·45 grams of sodium naphthionate), dissolved in water (400–500 c.c.), acidified with sulphuric acid, and nitrite solution run in till a reaction is obtained, after standing for five minutes, with starch iodide-paper. The number of c.c. of nitrite solution used, multiplied by 5, gives the percentage.

Anthracene.

M.P. 216·5°.

The valuation of commercial anthracene is carried out as follows:—1 gram of the sample is heated with 45 grams of glacial acetic acid in a flask of 500-c.c. capacity on a sand-bath. The flask is fitted with a reflux condenser about 75 cm. long, the top of which holds, by means of two rubber rings, a test-tube of about 50 c.c. capacity. A solution of 15 grams of crystallised chromic acid in 10 c.c. of glacial acetic acid and 10 c.c. of water is contained in the test-tube, and as soon as the contents of the flask are boiling the chromic acid solution is siphoned over from the test-tube into the condenser tube by means of a small capillary siphon. This is chosen of such a size that the chromic acid is siphoned over in about two hours. (This is tried beforehand.)

When the test-tube is empty, the flask is boiled for two hours longer, and allowed to cool till the following day. 400 c.c. of water are then added, and the whole filtered. The residue of anthraquinone is washed, first with cold water, then with boiling alkaline water, and finally with boiling water alone, until no alkaline reaction is obtained. The filter-paper is now carefully removed from the funnel, opened out on a glass plate, and the contents washed into a small porcelain dish and dried at 100°.

The crude anthraquinone is then heated to 100° with 10 grams of slightly fuming sulphuric acid for ten minutes, left till next day in a damp place, and washed into a dish with 200 c.c. of cold water. The precipitated anthraquinone is filtered off, washed with alkaline water, and finally with hot water alone; then washed into a small dish, dried, and weighed. The dish is then heated on a sand-bath until the anthraquinone has volatilised, and is again weighed. The last weight subtracted from the first gives the weight of the anthraquinone, which, multiplied by 85·57, gives the percentage of anthracene in the sample (Luck, *Ber.*, vi. 1347; see also Bassett, *Chem. News*, lxxiii. 178, lxxix. 157).

For the detection of methylanthracene, see A. G. Perkin, *J. Soc. Dyers*, 1897, p. 81; and of paraffin, Allen, *Comm. Org. Analysis*, 4th ed., vol. iii. p. 281.

Turkey-red Oil Analysis.

Primary test.—The oil must react slightly alkaline or neutral; mixed with water, a perfect emulsion must be obtained, from which oil-drops are separated after a few hours. These drops must be completely soluble in ammonia, otherwise unsaponified fat is present.

Water.—According to Stein, 10 grams of oil are melted with 25 grams dry paraffin wax in about 75 c.c. saturated salt solution. The cake is dried and weighed. The increased weight of wax represents oil free from water; the difference between 10 and the exact amount of oil used is water.

Fat (total).—100 c.c. of oil are mixed in a graduated cylinder with 20 c.c. hydrochloric acid (concentrated), and then made up with saturated salt solution to 500 c.c. The whole is shaken frequently and slightly heated. On cooling, the fat swims on the salt solution. The number of c.c. shows direct the total amount of fat. (This is sufficiently accurate for practical purposes.)

Addendum.—P. 300. The amount of free sulphur trioxide in fuming sulphuric acid can be accurately estimated by titrating a weighed quantity of the acid in a stoppered cylinder with water until no further fuming occurs when air is blown through a glass tube on to the surface of the liquid (Parker, *J.S.C.I.*, 1917, xxxvi. 692).

CHAPTER XXXI.

THE APPLICATION OF THE COLOURING MATTERS.

(1) The Behaviour of the Principal Fibres towards Reagents.

Before dealing with the application of the dyestuffs to the fibres on the experimental scale, it will be necessary to discuss briefly the more important properties of the textile fibres, since it is upon the nature of the fibre that its behaviour towards the colouring matters mainly depends.

The textile fibres may be classed under the following heads :—

I. Nitrogenous fibres are of animal origin, and the two most important members are wool and silk.

They are characterised by being readily disintegrated by alkalies, by which the non-nitrogenous fibres are unattacked; but are more resistant than these towards acids.

II. Non-nitrogenous fibres are of vegetable origin, and consist of cotton, flax, hemp, jute, etc.

The reactions of these two important groups are readily seen by the following table :—

Reagent.	*Nitrogenous* (Animal).	*Non-nitrogenous* (Vegetable).
Alkalies (**NaOH**, 12° Tw.), .	Dissolved.	Undissolved.
Acids (H_2SO_4 1 : 3), . .	Undissolved.	Dissolved.
Ignition, ...	Burns slowly, gives off a smell of burnt horn, and fuses to a small bead of hard porous carbon.	Burns rapidly, gives off a smell of burnt paper, and leaves behind a loose white ash.
Strong H_2SO_4 and iodine, .	Unaltered.	Stained blue.
Zinc iodochloride,* . .	Unaltered.	Stained violet.
Boiled with lead oxide and caustic potash	Blackens.†	Unaltered in colour.

* A concentrated aqueous solution of zinc chloride is added to a solution of iodine in potassium iodide, the following proportions being taken :—1 pt. **I**, 5 pts. **KI**, 30 pts. $ZnCl_2$, 14 pts. H_2O.

† Owing to the formation of lead sulphide, due to the presence of sulphur in the animal fibre.

(2) Experimental Dyeing.

The valuation of the individual members of the various groups of the synthetic dyestuffs is at the present time, with few exceptions, merely a matter of comparison with types, a comparison which is usually carried out either

(1) By colorimetric tests, or
(2) By comparative dye-trials.

In the first case the comparison is brought about by dissolving equal amounts of the samples under examination in water, and comparing the colour of the solution produced, in a specially devised apparatus known as the colorimeter.

In the second, equal weights of some fibre are dyed in solutions containing known quantities of the samples to be compared, under precisely the same conditions, and the difference in the resulting shades noted.

This second process is by far the most generally used, since it enables the dyer to ascertain the relative purity of any sample which he may wish to examine, and is, moreover, the only really reliable one, since the chemical analyses of dyestuffs, except in a few cases which will be dealt with later, cannot be accurately effected, owing to the many substances which occur in them as impurities, accidental or otherwise.

The knowledge, therefore, of the methods by which experimental dyeings may be produced on the fibre is essential, not only to the works chemist, but also to the research chemist, who may wish by its means to ascertain the relative importance of any colouring matter with which he may come in contact.

Again, the value of a dyestuff depends to a very considerable extent upon its behaviour towards reagents, both in the free state and upon the fibre. In the ensuing pages will be found tests by which their behaviour in this respect can be ascertained.

Standard solutions of dyestuffs.—In order to facilitate the employment of the small quantities of the colouring matters necessary in dye-trials, it is usual to prepare a standard solution of them.

The strength of this solution is naturally determined to a great extent by the nature of the dyestuff, its solubility in water, and its colour strength; but for most purposes a solution containing 1 gram in a litre of water will be found most convenient.

The dyestuff should first be dissolved to a clear solution in a small quantity of boiling water contained in a beaker, and then filtered (if necessary) into a litre flask and made up to bulk. It is advisable to use distilled water in making these solutions (see *Solubility*, p. 330).

The dye-bath.—The dye-bath is made by the addition of the requisite quantity of the standard solution of the dyestuff to a convenient quantity of water, which in the case of wool should be forty to fifty times the weight of the material, and in the case of cotton twenty-five times the weight of material dyed. To the dye-bath are also added the various substances (depending upon the nature of the dyestuff) which are required to enable the colouring matter to affix itself upon the fibre under the most suitable conditions.

The most frequently used of these should be kept in the laboratory in the form of standard solutions.

They are:—

Neutral sodium sulphate (Glauber's salt),	.	20 per cent.	solution.
Acid potassium sulphate,	.	10 „	„
Sodium carbonate,	.	10 „	„
Sulphuric acid,	.	10 „	„
Common salt,	.	10 „	„
Sodium phosphate,	.	10 „	„

Experimental dyeing can, if necessary, be carried out in beakers; but these should not be directly heated, but placed in baths containing either strong salt or calcium chloride solution.

The experimental dye-baths which are found in most technical laboratories are, however, the most suitable. They consist of porcelain beakers with lids, which are placed, usually in sets of three, in a copper bath, in which can be boiled either a solution of common salt or any other substance capable of giving the required temperature.

Wool dyeing.—For the purpose of the dye-trial 5 grams of pure wool is usually sufficient.

The wool should first be freed from greasy impurity by boiling in a bath containing a little ammonia for one to one and a half hours; it should then be dried and weighed accurately.

The quantity of dye solution taken should depend upon the nature of the dyestuff; in most cases a quantity representing 1 per cent. on the weight of the wool is the most convenient, although in others, when the colour strength of the dyestuff is weaker, 2 per cent. or even 3 per cent. is advisable.

In any case the quantitative dyeing, which is merely relative, should be adapted to the nature of the substance (where this is unknown) by a preliminary experiment.

The percentages mentioned are calculated on the weight of material dyed.

(1) *Acid dyestuffs.*—Prepare the bath with the necessary amount of dye, and 10 to 15 per cent.[1] potassium hydrogen sulphate, or 10 per cent. neutral sodium sulphate, with 3 to 5 per cent. sulphuric acid.

In some cases the fibre may be entered directly into the boiling bath, but it is usually advisable to enter in the cold and then gradually heat to boiling, the fibre being kept constantly in motion by means of a glass rod. The colour will be found to be quickly absorbed, and after boiling for one to one and a quarter hours will have been completely absorbed by the wool, which should then be well washed and dried on the hot cylinder.

Weak acid dyestuffs, such as the Eosines, etc., can be dyed in a bath containing 5 per cent. acetic acid, and the Rhodamines, although from their structure basic dyestuffs, can also be dyed in this way.

An exception to this method is Alkali blue, which fixes itself upon the wool fibre from an alkaline bath in the form of a bluish-grey compound, which subsequently yields the blue on treatment with acids. The following method should be adopted in this case:—

Dye in a boiling bath containing the dyestuff and 2 to 5 per cent. borax for one hour, then wash and develop in a bath containing 2 to 5 per cent. sulphuric acid at 50°; wash thoroughly and dry.

(2) *Basic dyestuffs.*—Prepare the bath with the requisite quantity of dyestuff and 10 per cent. of neutral sodium sulphate; enter the fibre cold, then heat to 90°, and maintain at this temperature until the bath is extracted; wash and dry.

(3) *Substantive cotton dyes.*—Dye in a boiling bath containing 10 per cent. neutral sodium sulphate; wash and dry.

Many of the substantive cotton dyes are better adapted for the dyeing of wool than of cotton.

(4) *Mordant dyestuffs.* — (*a*) *Mordanting before dyeing.* — Mordant the weighed wool by treating it in a bath containing 3 per cent. bichromate of potash and 2½ per cent. acid potassium tartrate (tartar), entering at 60° and gradually raising to boiling, then keeping it at this temperature for one hour; wash and dye in a bath containing the requisite quantity of the mordant dyestuff, entering cold and raising the temperature very slowly to the boiling-point, maintaining it at this temperature for one hour; wash and dry.

[1] Percentages refer throughout to the weight of fibre taken.

(*b*) *Mordanting after dyeing.*—Dye as an acid dyestuff, and subsequently treat in a fresh bath containing 1½ to 2 per cent. of bichromate of potash, together with a little acetic acid.

This method only applies to those dyestuffs—such as azo-compounds containing salicylic acid, etc., as components—which are acid as well as mordant dyestuffs.

Silk dyeing.—*Purification of silk.*—The purification of silk consists in removing the sericine and colouring matters present in the raw material. As, however, these mainly reside in the last layer surrounding the fibre, all that is necessary is to remove this by the process known as scouring.

This process entails considerable loss in the weight of the silk, being 18 to 22 per cent. in the case of Chinese and Japanese silks, and as much as 25 to 30 per cent. in the case of European silks.

It is effected by boiling the raw material in two successive baths containing a solution of soap, usually 25 to 30 per cent. in the first and 20 per cent. in the second.

The process in the first bath usually requires ten to fifteen minutes, and in the second about the same time, the temperature being maintained throughout at about 100°.

When finished, the fibre should exhibit its characteristic lustre, and should remain soft to the touch after drying.

Since silk loses its characteristic "handle" on treatment with alkalies, this must be restored after the scouring process, by passing it through a bath containing 1 to 2 per cent. sulphuric acid.

The soap solution containing the sericine, which can be used several times, is subsequently employed in the dye-bath as "boiled-off liquor" or "bast soap."

The weight of the silk sample should be taken after the scouring process and subsequent treatment with acid.

(1) *Acid dyestuffs.*—Dye at 90° in a "boiled-off liquor" bath acidulated with sulphuric acid.

Prepare the bath by adding the requisite quantity of dye solution, using boiled-off liquor in the place of water, then add sufficient dilute sulphuric acid to give a marked acid reaction, enter the fibre cold and then gradually raise to the above temperature, maintaining at this for three-quarters to one hour. The silk must be thoroughly worked throughout the operation. After dyeing, pass through a bath containing a small quantity of sulphuric acid.

(2) *Basic dyestuffs.*—Dye in the same way in a boiled-off liquor bath containing the requisite quantity of dye solution slightly acidified with acetic acid. The temperature should be raised to 80°, and maintained at this until no more dye is absorbed. After dyeing, wash and pass through acidulated water.

(3) *Substantive cotton dyestuffs.*—Enter the fibre cold and then dye, boiling with an addition of 15 per cent. neutral sodium sulphate and 5 per cent. soap. After dyeing, pass through dilute acid; wash and dry.

Cotton dyeing.—

I. Substantive Cotton Dyestuffs.

The dyeing of cotton with these dyestuffs is brought about by heating the weighed material in a slightly alkaline bath containing the required quantity of dye solution (usually 3 per cent.), together with a quantity of sodium chloride, depending upon the quantity of the colouring matter and its affinity for the fibre.

Thus colouring matters which do not exhaust readily—that is, are not extracted readily by the fibre from the bath—require a proportionately large amount of salt.

Care must be taken, however, not to add too much salt, otherwise the dyestuff may be precipitated from its solution and cause unevenness in the dyeing.

A typical example may be given as follows:—Enter the cotton into a bath containing 20 per cent. neutral sodium sulphate, 2 per cent. sodium carbonate, and 30 per cent. sodium chloride at 60°, then heat gradually to boiling, and maintain at this temperature until no further absorption takes place (usually one to one and a half hours).

All dyeings on cotton with the substantive cotton dyes are more or less fugitive. Their fastness may be increased by the following processes:—

(1) Diazotising and developing.
(2) After-treatment with copper sulphate.
(3) After-treatment with bichromate of potash and copper sulphate.

(1) **Diazotising and developing.**—This method applies only to those substantive cotton dyes that contain a diazotisable amido-group; it is carried out as follows:—

The dyed material is passed through a bath containing

1 gram sodium nitrite (previously dissolved in water),
2½ c.c. sulphuric acid, 168° Tw. (sp. gr. 1·84),
} made up to 1 litre,

in which it should be worked for fifteen minutes, then rinsed and immediately entered into a cold solution of the developer.

The following developing baths can be used according to the shade desired:—

5 grams β-naphthol,
5 „ caustic soda, 76° Tw. (sp. gr. 1·38),
1 litre of water;

5 grams resorcinol,
10 „ caustic soda, 76° Tw. (sp. gr. 1·38),
1 litre of water;

and

5 grams toluylenediamine hydrochloride,
10 „ crystalline sodium carbonate,
1 litre of water,

the diazotised material being worked in the bath for about fifteen minutes, then washed and dried.

(2) **After-treatment with copper sulphate.**—Many substantive cotton dyes are rendered faster if their dyeings are subsequently treated with a solution of copper sulphate, although in many cases the shades are considerably deteriorated thereby.

The process consists in passing the dyed material through a bath heated to 100° containing 3 per cent. sulphate of copper solution.

The treatment should last half an hour.

(3) **After-treatment with bichromate of potash and copper sulphate.**—The addition of bichromate of potash in some cases yields better results than sulphate of copper alone. The following bath may be used :—

·5–1 per cent. bichromate,
1·5–3 „ copper sulphate,
·5–1 „ acetic acid, 30 per cent.,
} on the weight of material.

The after-treatment can also be applied to diazotised and developed dyeings.

II. Dyes Developed Directly on the Cotton Fibre.

To this class belong certain insoluble azo-compounds which are produced by immersing the fibre impregnated with a second component in a bath containing a solution of the diazo-salt of the first component.

A typical example is *p*-Nitraniline red, which is produced by combining β-naphthol (on the fibre) with diazo-*p*-nitraniline chloride.

Treating with β-naphthol.—The cotton is passed through the following solution (for 10 grams of cotton) :—

10 grams β-naphthol,
10 „ caustic soda solution, 77° Tw. (sp. gr. 1·385),
100 c.c. boiling water,
25 grams Turkey-red oil,
100 c.c. boiling water,

mixed together and diluted to 1 litre.

It should be thoroughly worked for from five to ten minutes in the lukewarm liquid (40°), then wrung out and dried in the drying cupboard by means of hot air. When thoroughly dry, the fibre should be developed without loss of time, since it rapidly becomes brown on exposure.

Developing.—

Solution A.

15 grams *p*-nitraniline are mixed with
36 c.c. boiling distilled water, and dissolved with
32 c.c. hydrochloric acid, 32° Tw. (sp. gr. 1·16).
This acid solution is run in a thin stream with constant stirring into
225 c.c. of water, which should be cooled by means of lumps of ice.
The *p*-nitraniline hydrochloride separates out in the form of fine yellow crystals.
After the solution has cooled to not more than 12°,
8 grams of nitrite of soda dissolved in
24 c.c. of cold water are poured in, and after remaining ten minutes the whole diluted to
400 c.c. with cold water.

Solution B.

8 c.c. caustic soda solution, 77° Tw. (sp. gr. 1·385), are diluted with cold water to
76 „ and mixed with a solution of
20 grams acetate of soda in
76 c.c. of cold water.

The developing bath is made by mixing 7 parts of solution A with 3 parts of solution B, the solution being kept cold by means of ice.

The dye is formed by passing the prepared cotton, which should be quite dry, through the developing solution, in which it should be worked for about one minute, then wrung out and again worked for one minute, after which it should be thoroughly rinsed, and finally washed in a boiling soap solution.

III. Basic Colouring Matters on Cotton.

The property possessed by the basic colouring matters of forming insoluble lakes with tannic acid is taken advantage of in dyeing them on the cotton fibre.

The process consists in first treating the fibre with tannic acid, upon which it is fixed by means of tartar emetic, and then steeping the cotton thus mordanted in a solution of the basic dyestuff.

Mordanting: Tannic acid solution.—The cotton is worked in a bath containing 2½ to 5 per cent. of tannic acid (on the weight of material) at a temperature of 50° for about fifteen minutes, after which it is allowed to remain in the bath for six hours.

Without rinsing, it is then worked for one-quarter of an hour in a cold bath containing 2½ per cent. tartar emetic or 1½ per cent. fluoride of antimony, after which it should be thoroughly washed and wrung out.

In each case the quantity of solution should be adapted to the quantity of fibre; for 10 grams 500 c.c. will be found a convenient amount.

Dyeing.—Enter the mordanted fibre into a cold solution of the requisite quantity of dyestuff, and work whilst slowly raising the temperature to 70°; keep at this temperature until all colouring matter has been absorbed.

The fastness of the colour can be increased by subsequently passing the dyed material through the tannic acid solution.

Certain basic dyestuffs—for example, the Rhodamines—give only poor shades of colour on tannin mordant. The brilliant pink colour of these dyestuffs can, however, be produced on cotton by using a mixed mordant of Turkey-red oil and aluminium acetate in the following way:—

Mordanting.—Work the fibre for fifteen minutes in a solution containing 1 part of Turkey-red oil and 9 parts of water, wring out and dry in hot-air cupboard; then pass several times through a solution of acetate of alumina, 10° Tw., wring out and dry. Both operations should then be again repeated in the same manner.

Dyeing.—As above.

IV. Acid Colouring Matters on Cotton.

The acid colouring matters (except the substantive cotton dyes) are not well adapted for the dyeing of cotton. A fugitive colour can, however, be produced by dyeing in a concentrated bath containing alum or stannic chloride.

The Eosines, etc., can be dyed upon cotton from a bath containing a large quantity of common salt.

V. The Sulphur Dyestuffs on Cotton.

The cotton fibre is dyed with these dyestuffs from a bath containing them dissolved in a solution of sodium sulphide.

The bath is prepared by boiling a solution containing the requisite quantity of solid dyestuff, 2 to 3 per cent. sodium carbonate, 5 to 10 per cent. crystallised sodium sulphide, and 10 per cent. sodium chloride or Glauber's salt. The fibre is entered into the boiling bath and worked until finished.

It is essential that, after dyeing, the cotton should be thoroughly washed before drying.

The fastness of the sulphur colours may be increased by after-treatment with chromium or copper salts, where such treatment does not affect the shade.

Cloth, after dyeing with sulphur colours, is often padded with sodium acetate in order to prevent tendering should sulphuric acid be subsequently formed on the fibre.

The shade of most sulphur colours is brightened by after-treatment with peroxide of hydrogen or sodium, but the fastness is diminished by this process. Certain blue blacks, for example, can be converted into Navy blues by this treatment.

VI. The Production of the Vat-Colours on Cotton and Wool.

The most important dyestuff of this class is Indigo, which is produced upon the fibre by first treating it with an alkaline solution of Indigo white, which, on oxidation in the air, is reconverted into the blue.

The term "vat" applies to the vessel employed for dissolving the Indigo, and also to the solution itself, which may be prepared by the aid of various reducing agents.

Two only need be considered here—

(1) The zinc vat for cotton.
(2) The hydrosulphite vat for wool and cotton.

The zinc vat for cotton.—

50 grams Indigo (20 per cent. paste).
10 „ zinc dust.
30 „ unslaked lime.

Mix the zinc dust with 120 c.c. of water at 50°; add the Indigo paste, and then the lime with constant stirring. The whole is left to stand for five to six hours, but is stirred from time to time. The reduction is complete when a drop of the solution placed upon a sheet of glass runs off as a yellow liquid which oxidises in the air in the course of forty to fifty seconds.

The reduced solution is then diluted with 500 c.c. of water, and the cotton fibre dyed in it by being thoroughly soaked, wrung out, and dried in the air.

The process is repeated until the requisite shade of blue is obtained.

The "hydrosulphite" vat (for cotton).—This vat is based on the property of hyposulphurous acid, $H_2S_2O_4$, discovered by Schützenberger, of forming with Indigo a colourless double compound which is soluble in alkalies, and is decomposed by the weakest oxidising agents, Indigo blue being thereby liberated.

For practical use the sodium salt of hyposulphurous acid, $Na_2S_2O_4$, is prepared by allowing zinc dust to act on sodium bisulphite solution in a tightly closed vessel, the mixture being kept stirred and cooled. The reaction is usually complete within four to five hours.

The hydrosulphite solution is rendered slightly alkaline with milk of lime, in order to diminish its instability, and is then ready for use.

Preparation of the hydrosulphite solution.—

100 parts of sodium bisulphite solution, 71·4° Tw. (sp. gr. 1·358), are diluted with
225 „ of cold water, and in the course of half an hour
8¾ „ of zinc dust stirred into this solution. The whole, which is stirred from time to time, is left to stand four to five hours, and then mixed with
11½ „ of lime slaked in
30 „ of water.
After allowing the sediment to settle, the clear solution is decanted and
7 „ caustic soda solution, 36° Tw. (sp. gr. 1·18), added.

The hydrosulphite solution is now ready for use, and should be kept in a well-closed vessel in a dark room.

It should show a specific gravity represented by 19–20° Tw. (sp. gr. 1·095–1·1).

Hydrosulphite vat.—

5 parts Indigo (20 per cent. paste) are mixed with
3 „ hot water; to this mixture
8½ „ caustic soda solution, 76° Tw. (sp. gr. 1·38), are added, and the whole well stirred; after heating to 50°,
25 „ of hydrosulphite solution, 20° Tw. (sp. gr. 1·1) are added, and the temperature kept at 50°.

In the course of the reduction which takes place, and which is tested in the usual way with a sheet of glass, more hydrosulphite solution is added in several portions. The reduced Indigo ought to run off the sheet of glass as a yellow liquid which oxidises in twenty to thirty seconds.

The cotton fibre is then dyed in the same manner as indicated in the case of the zinc vat.

The hydrosulphite vat (for wool).—The process is essentially the same, only the use of caustic soda in the above preparations must be replaced by milk of lime. Thus the hydrosulphite solution is rendered alkaline by the addition of the requisite quantity of milk of lime, and the vat is prepared by treating 5 parts Indigo (20 per cent. paste) with 4 parts hydrosulphite solution at 80°. Of the resulting yellow-brown solution, a definite quantity, depending on the depth of blue desired, is added to the vat, together with more hydrosulphite solution.

Wool is dyed in this vat at 50–60°, a temperature that must not be exceeded by more than a few degrees.

VII. The Mordant Dyestuffs on Cotton.

Essentially this process consists in first mordanting the cotton fibre by steeping it in a solution of the acetate of some metal, which, on subsequent steaming, remains on the fibre in the form of the oxide or hydroxide.

The cotton thus mordanted is then boiled in an aqueous solution or emulsion of the mordant dyestuff, when the corresponding metallic lake is precipitated on the fibre.

Another process consists in precipitating the hydroxides upon the fibre in the form of insoluble tannates or fatty-acid salts, by first steeping the cotton in tannic acid or fatty acid, and then treating it with the metallic salt used as a mordant.

The more important mordants for cotton are:—

I. Alumina mordants,
II. Iron mordants,
III. Chrome mordants, and
IV. Tin mordants.

I. Alumina mordants.—The most usual form in which this mordant is applied to the cotton fibre is as aluminium acetate, which is prepared either by dissolving aluminium hydroxide in acetic acid or by decomposing alum or aluminium sulphate with lead acetate.

It is immaterial whether aluminium potassium sulphate (alum), $Al_2(SO_4)_3.K_2SO_4$, or the normal aluminium sulphate, $Al_2(SO_4)_3$, is used in this preparation; the only point about which it is necessary to be certain is that no iron is present as impurity.

The following is a method for preparing a solution of aluminium acetate, 9° Tw.:—

Dissolve 500 grams of lead acetate in
500 c.c. of boiling water, and mix it hot with a solution containing
505 grams aluminium sulphate (free from Fe) dissolved in
500 c.c. of boiling water.

Allow the precipitated lead sulphate to settle, decant clear liquid, and dilute until it shows a specific gravity of 9° Tw. (sp. gr. 1·045).

For use as a mordant it is unnecessary that the whole of the sulphuric acid present in aluminium sulphate should be precipitated; in fact it is preferable in practice to select for the preparation those proportions which would produce a sulphacetate according to the equation

$$Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 \rightarrow Al_2SO_4(C_2H_3O_2)_4 + 2PbSO_4$$

Turkey-red upon cotton.—The name Turkey-red is applied to the colour produced upon cotton by the aid of Alizarine, alumina, lime, and fatty-acid compounds. A considerable amount of work has been done upon the nature and formation of this colour lake. Rosenstiehl first found that the formation of the lake from Alizarine and alumina could not take place except in the presence of lime; this was subsequently confirmed by Liechti and Suida, who found that all Turkey-red dyeings contain lime.

According to Liechti and Suida a "normal red" has the composition $Al_2O_3.CaO(C_{14}H_6O_3)_3$.

The part played by the fatty acids in Turkey-red dyeing has not yet been clearly defined.

Turkey-red oil is prepared by treating olive oil or castor oil with concentrated sulphuric acid, usually 3 parts of acid being added to 10 parts of oil.

The acid is slowly poured into the oil with constant stirring, and the whole then left to stand until a sample of the product is found to dissolve completely in water, whereupon it is poured into water and washed with a solution of sodium chloride until free from sulphuric acid.

During the process of mixing, the temperature should not be allowed to rise above 40°, otherwise a copious evolution of sulphur dioxide will ensue, and the product will be dark in colour and furnish poor results on dyeing.

Dyeing.—The production of a good Turkey-red upon cotton can only be attained by practice; the following directions should, however, yield fairly good results if carefully followed.

Cleaning.—Free the cotton fibre from grease, etc., by boiling it in a weak solution of sodium carbonate; wring out thoroughly.

Oiling.—Without drying, enter into a bath containing

10 parts Turkey-red oil,
90 „ water,

and work until thoroughly soaked. Wring out and dry in the hot-air cupboard at 40–50°.

Repeat this treatment twice, drying between each immersion.

Alumina mordant.—Work the fibre thoroughly in a bath of aluminium acetate, 9° Tw. (sp. gr. 1·045); wring out and dry at 40–50°.

Repeat this treatment.

Chalking.—Enter the cotton into a bath containing

6 grams of chalk and
1 litre of water

at 30–40°. Stir well for about half an hour, and then wash thoroughly in clean water. It is unnecessary to dry the cotton before dyeing.

Dyeing.—The water used should show two to three degrees of hardness; the quantity of dyestuff should be 1·5 grams of Alizarine (20 per cent. paste) for 10 grams of cotton.

Stir the dyestuff into the water and enter the cotton at 20–25°. Work the fibre at this temperature for about twenty minutes, and then heat up so that in about half an hour the temperature rises to 60°. Keep at this point for about an hour, then wring well and dry.

Steaming.—Steam the dried cotton for one hour at a pressure of one atmosphere, or for two hours without pressure; then wash well.

Brightening.—Brighten the dyed material in a closed apparatus at a pressure of half an atmosphere; use a solution containing 4·5 grams of soap in 1 litre of water; leave the cotton in it for ten minutes, and wash well.

This process may be simplified by heating the dye-bath to boiling; subsequent steaming then becomes unnecessary.

The brighter shades of red are, however, obtained at the lower temperature.

II. Iron Mordants play a most important part in black dyeing with logwood, and also in the production of Alizarine violet.

The cotton fibre can be mordanted with iron by steeping it in ferrous sulphate solution and subsequently passing it through a solution of tannic acid.

It is, however, more frequently mordanted by means of iron pyrolignate.

This substance is prepared by dissolving scrap-iron in crude pyroligneous acid; it consists for the most part of ferrous acetate. This compound, however, in the pure state is not a good mordant for cotton, being too readily oxidised, and, consequently, liable to be poorly fixed on the fibre.

The pyrolignate, on the other hand, forms a good mordant, owing to the presence of impurities in it, which retard the oxidation of the acetate.

The following indicates a method of producing Alizarine violet on the cotton fibre:—

Work the material thoroughly in a bath containing

3 grams of tannic acid in
1 litre of water;

wring and pass through a bath of

pyrolignate of iron, 3° Tw. (sp. gr. 1·015).

After washing, dye in the same manner as given in the case of Turkey-red.

III. Chrome mordants.—At the present time the chrome mordants are the most important in use, many dyeings formerly mordanted with alumina or iron being now treated with chromium salts; and, with the exception of a few Alizarine dyes, all artificial mordant dyestuffs are fixed with chrome mordants exclusively.

These mordants differ greatly in behaviour from the iron and alumina mordants, being, on the one hand, more difficult to dissociate, and therefore harder to fix on the fibre; whilst, on the other hand, the combination with the fixed chromium hydroxide—that is, the formation of the lake—is effected more readily.

The chromium acetates are so difficult to decompose that they cannot be used like the acetates of iron and alumina.

The most usual chrome mordants are the following:—Chromium acetate, bisulphite, fluoride, basic chloride, potassium and sodium bichromate, and chromic chromate.

Chromium acetate is produced by double decomposition from chrome alum and lead acetate. Here, as in the case of aluminium acetate, the main product consists of a sulphacetate.

Solutions of chromium acetate, which, when first prepared, are green, tend by long keeping to become violet.

It is assumed that the violet solution contains neutral salt, whilst the green solution consists of mixtures of acid and basic salts. The former are more difficult to decompose.

Chromium bisulphite is prepared by treating a solution of chrome alum with an excess of sodium bisulphite; it is largely used in the mordanting of cotton.

Chromium fluoride is used more especially for the mordanting of wool.

A basic chromium chloride may be prepared by dissolving chromium hydroxide in chromium chloride, and is used for mordanting silk and cotton.

The mordanting of cotton by this reagent can be effected in two ways:—In one, the yarn is impregnated with the mordant solution, dried, and passed through a boiling solution of sodium carbonate. In the other, the hydroxide is fixed by the aid of tannin or oleic acid.

Potassium bichromate is largely used as a mordant, but its use is restricted to wool.

Chromic chromates are found in commerce under the names Chrome mordant GA I., GA II., and GA III. of the Höchst Manufactory [M], and are suitable for mordanting cotton. The following method is recommended by these manufacturers:—

For 10 grams of cotton.

1. *Boiling.*—The fibre is boiled in a solution containing 3 grams of sodium carbonate in 500 c.c. of water.

2. *Mordanting.*—The well-wrung-out yarn is worked cold in chrome mordant GA I., 19° Tw. (sp. gr. 1·095), for half an hour, then steeped in this mordant for twelve hours and wrung out.

3. *Fixing.*—The mordanted fibre is fixed by working it in a 2 per cent. solution of sodium carbonate at 50° for three-quarters of an hour, and then well washed.

4. *Dyeing.*—The dye-bath is made up as follows:—

14 grams of dyestuff (20 per cent. paste),
6 „ ammonia, 25 per cent.,
2 „ tannic acid,
500 c.c. water,

in which the fibre is worked for a quarter of an hour in the cold; then 14 grams of acetic acid (12° Tw., sp. gr. 1·06) are added and the cotton worked for another quarter of an hour, after which the temperature is slowly raised to the boil within one hour, and the dyeing operation continued at this temperature for a further period of one hour.

Tin mordants.—As independent mordants the tin compounds are of inferior importance.

The chief salts used are stannous chloride (salts of tin), stannic chloride, and sodium stannate.

Stannous chloride is the most important tin mordant for wool, and stannic chloride for cotton and silk.

The latter is fixed upon the cotton fibre with the aid of tannic acid.

Sodium stannate is frequently styled "preparing salt," owing to its employment in preparing fabrics for printing. Its chief use is in the printing of wool.

VIII. Colours Produced Directly upon the Fibre by Oxidation.

Aniline black, the typical member of this group, is produced directly on the cotton fibre by the oxidation of aniline, and the two following methods will suffice to indicate the manner in which dyestuffs of this kind are formed :—

I. One bath black—

The bath should contain

5 per cent. aniline.
12 „ hydrochloric acid.
6 „ bichromate of soda.
5 „ copper sulphate.

The cotton should be entered into the cold bath and worked for one hour; then the bath should be raised to boiling during another hour, and the fibre worked at this temperature for a further half hour; wash and dry.

II. Oxidation black—

126 grams aniline hydrochloride are dissolved in
300 c.c. of water, and mixed with
40 grams chlorate of soda,
150 „ acetate of alumina, 21·6° Tw. (sp. gr. 1·107),
5·7 „ ammonium chloride,
3 „ copper sulphate,

and the whole made up to 1 litre.

The fibre is thoroughly impregnated in this solution, wrung out and dried. It is then worked for half an hour at 60° in a bath containing

2·5 per cent. bichromate of soda,
·5 „ aniline hydrochloride,
·2 „ sulphuric acid, 161·8° Tw. (sp. gr. 1·809),

and then well washed and dried.

CHAPTER XXXII.

THE VALUATION OF A COLOURING MATTER.

In order to determine the relative value of any particular dyestuff, the following facts have to be taken into consideration :—

(1) Its solubility in water.
(2) Its equalising power.
(3) Its behaviour on the fibre towards various physical and chemical influences which appear during the process of manufacture and in the daily use of the dyed material.

Solubility.—This depends not merely upon the nature of the colouring matter, but also upon the condition of the water.

Many dyestuffs form insoluble compounds with lime; and, therefore, if the water is hard, a portion will be precipitated owing to the formation of these insoluble bodies, and in these cases the hardness of the water should be corrected by the addition of sulphuric, acetic, or oxalic acids or sodium carbonate, according to the nature of the colouring matter dissolved.

The solubility of a pure dyestuff can be readily determined by evaporating a measured quantity of its concentrated aqueous solution to dryness in a weighed platinum vessel.

If, however, impurities are present, such as, for example, sodium chloride, this method would give unsatisfactory results, because in making a saturated solution by the usual process of filtering the aqueous solution from excess of undissolved colouring matters, an undue proportion of the more soluble salt would be present in the solution.

Since most commercial colouring matters contain inorganic impurities, it is advisable when dealing with the industrial product carefully to prepare a solution which is just saturated and which does not contain any undissolved material.

Equalising power depends, in the case of woollen fibres, upon the affinity of the colouring matter for the fibre.

The greater or less the affinity, the more quickly or slowly the dye-bath is exhausted.

Colours which are absorbed rapidly do not, as a rule, dye evenly, but are generally faster to washing; whilst colours which are only slowly taken up by the fibre yield more even dyeings.

The rapidity with which wool colours are absorbed by the fibre depends on the amount of acid in the dye-bath. Some colours require much more acid than others, but all may be made to dye quickly if the bath is sufficiently acid. There are probably very few good equalising colours which will dye from a neutral or nearly neutral bath, and, indeed, it may be stated that the amount of acid required to exhaust the dye-bath is a guide to the equalising power of the colouring matter.

The addition of sodium sulphate (Glauber's salt) to the dye-bath usually has the effect of preventing the too rapid absorption of a colouring matter possessing strong affinities for the wool fibre.

The following experiment (v. Georgievics, *Chemical Technology of the Textile Fibres*, Eng. trans., p. 134) will indicate roughly the equalising power of a dyestuff:—

Dye a sample of the fibre in the requisite quantity of the solution of a dyestuff to dye it, say, 2 per cent.; but, in the first instance, bind a portion of the fibre in such a manner that the bound portion does not come in contact with the dye solution.

When equilibrium has been attained, unbind the bound portion and again immerse in the dye-bath; if the dyestuff had good equalising properties, the portion which has been bound will rapidly assume the same colour as the other portion of the fibre, and, after a short boiling, will be indistinguishable from it.

If, however, the dyestuff has not good equalising power, the portion previously bound will remain lighter in shade than the surrounding fibre.

In the case of cotton fibres, level dyeing appears to be entirely a function of the solubility.

Fastness.

The behaviour of the colouring matters on the fibre towards chemical and physical influences, or, in other words, their fastness, depends not alone upon their nature, but also upon the nature of the fibre and the method of dyeing employed, so that one and the same colouring matter, dyed upon different fibres, or in accordance with different methods upon the same fibre, may show very different properties.

Fastness to light.—Upon this most important property depends largely the usefulness or otherwise of any particular colouring matter.

Dyes which show an extreme sensitiveness to light are useless, or can only be used to a very limited extent. The red, yellow, brown, and black dyes, as a rule, surpass the green, blue, and violet dyes in this respect.

Amongst the former are a number which will withstand an exposure of several summer months almost without change; the latter show, however, a greater inclination to fade.

The basic dyes are, on the whole, fugitive to light; but, on the other hand, there are among the acid dyes and the substantive cotton dyes products showing extraordinary resistance against the action of light, surpassing in this respect many of the natural colouring matters.

The fastness of any particular dyestuff to light can be determined by exposing samples dyed with it in photographic printing frames to the action of sunlight, half of the dyed fibre being covered by some non-translucent material, and a standard of known resistance to light being exposed at the same time.

A comparison of the covered and the uncovered portions with the standard will determine the relative light-fastness of the dyestuff in question.

Fastness to washing and milling.—In an examination of a colouring matter with regard to these properties, not only the alteration in shade, but also their "bleeding" into white or coloured material must be taken into consideration.

The degree to which a colour bleeds is not directly proportional to the amount which it loses in depth, but depends rather upon the affinity of the dye in question for the fibre washed simultaneously.

Thus many acid wool dyes, which lose much colour when washed, bleed some-

what on to the wool fibre, but not, or only very slightly, on to the vegetable fibre.

On the other hand, the substantive colouring matters, if they are not after-treated according to one or another of the methods stated above, without exception bleed into white cotton, even though these often lose very little colour on washing.

Washing test.—The pattern is plaited or mixed with undyed material, worked for about five minutes in a soap solution containing 5 grams of soap in 1 litre of water at 40°, and then allowed to remain in the solution for about fifteen minutes. It is then rinsed in clean water and dried.

A more severe test would consist in adding sodium carbonate to the soap bath, and using a higher temperature.

Milling test—for cotton—is the same as for washing, only more severe, using a bath containing 12 grams of soap in a litre of water.

For wool.—Plait together with undyed material and knead for twenty minutes at 50° in a solution containing 5 grams of soap and 4 grams of sodium carbonate in a litre of water. Allow to lie for ten minutes; rinse and dry.

Fastness to alkalies.—As dyed cotton goods are at the present time frequently mercerised, the fastness to alkalies of the substantive cotton dyes is a matter of some importance.

Alkali test.—Moisten the dyeing with concentrated or dilute alkalies, or moisten with milk of lime; allow to dry and brush off.

Fastness to acids and cross dyeing is estimated not only according to the resistance of the dyeings when coming into contact with acids, but also according to the degree in which interwoven material is stained when treated in a boiling acid bath.

All acid dyes naturally withstand a treatment in a slightly acid bath, and are generally faster to acids than the substantive and basic colours.

Amongst the substantive colours the reds were formerly the most sensitive to the action of acids, but at the present time there are many fast cotton scarlets.

The fastness to perspiration is a very much more severe test than fastness to acids. The only satisfactory test is a practical one, but the following process is frequently used to determine the resistance of a colouring matter:—

Perspiration test.—

100 grams common salt.
100 c.c. acetic acid.

Make up to one litre.

Impregnate the dye patterns together with white wool and white cotton. Roll up tightly together, and place in a well-closed incubator for twenty-four hours at 40° C.

Fastness to carbonising.—In addition to other impurities, sheep's wool frequently contains vegetable fragments which cannot be removed by washing. When this is the case, the vegetable matter is removed by the process known as carbonising, which consists in treating the material with dilute acid, drying, and finally removing the excess of acid by means of cold caustic soda.

As already mentioned, the vegetable fibres are disintegrated by the action of acids, and hence, after the wool has been treated in the above manner, any vegetable substances originally in it can be removed by mechanical means.

It is therefore sometimes of advantage that a wool dye should be unaltered by the carbonising process.

Test for fastness to carbonising.—Saturate the dyeing with a 5 per cent. solution of sulphuric acid, wring out and dry between undyed woollen material at about 100°; then pass through a cold solution of caustic soda, 6° Tw., rinse and dry.

Fastness to stoving.—The resistance of a dyestuff to the action of sulphurous acid comes into consideration almost exclusively for wool dyes, and only in exceptional cases for other colours, such as, for instance, when a material composed of a mixture of animal and vegetable fibres is to be subjected to stoving after the dyeing process.

Stoving test.—Allow sulphurous acid fumes to act directly upon the dyed material for twelve hours.

Fastness to bleaching.—The action of chlorine is so powerful that only a comparatively limited number of colouring matters are capable of withstanding it.

Wool is only in exceptional cases—*i.e.* in the production of a silky scroop—subjected to a treatment with chlorine.

In the manufacture of cotton goods, on the other hand, a subsequent improvement of the whites or bleaching of raw interwoven fibres often requires a more or less powerful treatment.

Bleaching test.—Treat the dyed material for fifteen minutes in a solution of bleaching-powder of $\frac{1}{4}$° Tw. (sp. gr. 1·001).

CHAPTER XXXIII.

THE ANALYSIS OF DYESTUFFS.

I. Quantitative Analysis.

In only a few instances is it possible to obtain quickly and accurately a quantitative estimation of the dyestuffs by purely chemical means. The fact that, for the most part, the commercial dyestuffs are not pure products, but are frequently mixtures of different dyestuffs or single dyestuffs mixed with substances like glucose, sodium sulphate, etc., renders their quantitative estimation a long and tedious process.

Chemists, therefore, usually rely upon the comparative dye-trial in order to obtain an appreciation of any product with which they may have to deal.

There are, however, certain methods by which some of the groups of dyestuffs can be quantitatively estimated, and these will be described in the following pages.

Azo-dyestuffs.

Reducing agents, such as zinc dust and water, zinc dust and ammonia, or caustic soda, zinc dust and dilute acid, tin and hydrochloric acid, stannous chloride, titanous chloride, etc., split the azo-compounds at the point of union of the two nitrogen groups of the chromophore, yielding

(1) The base from which the azo-compound was derived.
(2) The amido-derivative of the second or other components containing the amido-group in the position previously occupied by the azo-group.

Thus amidoazobenzene yields on reduction aniline and *p*-phenylenediamine

$$\begin{matrix} C_6H_5N & : & NC_6H_4NH_2 \\ H_2 & : & H_2 \end{matrix}$$

$$\swarrow \qquad \searrow$$

$$C_6H_5NH_2, \quad H_2NC_6H_4NH_2$$

The reduction of the azo-compounds can be used to a certain extent as a means of identifying them, and also by the method of E. Knecht (see later) for their volumetric estimation.

Owing, however, to the fact that the technical azo-dyes are rarely homogeneous substances—that is to say, they are rarely pure specimens of the compound they pretend to be—and also to the fact that they are frequently admixed with sodium sulphate, dextrine, etc., care must be taken in carrying out this method.

It is possible, however, in many cases to gain a fairly clear insight into the nature of an azo-dyestuff by studying its behaviour on reduction with zinc dust and alkali.

If the first component is a base volatile with steam (aniline, xylidine, etc.), it can be separated from the reduction mixture by distilling it with steam, and can be readily detected in the distillate by conversion into its acetyl derivative.

If, on the contrary, it is a base non-volatile with steam (benzidine, etc.), it will, if soluble, pass through on filtering the reduction mixture; or, if insoluble, it can be extracted from it by means of alcohol.

Witt (*Ber.*, 1888, xxi. 3471) recommends the following method :—

One gram of the purified dyestuff (recrystallised from water) is dissolved in the requisite quantity of boiling water (about 10 c.c.).

As soon as it has dissolved to a clear solution, it is removed from the sand-bath and treated with 6 c.c. of the reducing solution, which should consist of 40 grams stannous chloride dissolved in 100 c.c. pure hydrochloric acid (sp. gr. 1·19).

The reduction usually takes place immediately, frequently with violent ebullition, and the liquid rapidly becomes colourless.

The subsequent method of procedure depends upon the nature of the azo-compound reduced.

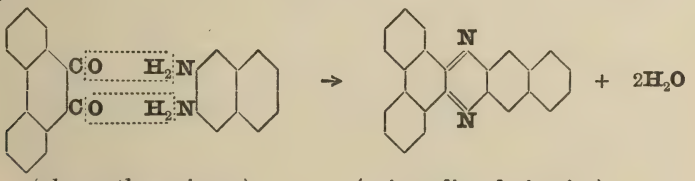
Bases, such as aniline, remain in solution as their hydrochlorides; amido-sulphuric acids remain partially or wholly in the residue with the amido-derivative of the second component.

In every case preliminary experiments must be tried in order to determine the best means of isolating the various products of the reaction.

A valuable means to the end is the formation of the quinoxaline derivative.

These substances are formed by the combination of phenanthraquinone and an *ortho*diamine.

Thus



(phenanthraquinone), (quinoxaline derivative),

and are usually well-defined crystalline compounds which frequently give characteristic colours with concentrated sulphuric acid.

Thus azo-compounds which contain naphthylamine sulphuric acids as second components, and which, therefore, yield *ortho*diamido-derivatives of naphthalenes on reduction, can be identified by converting the latter into its quinoxaline derivative by treating the filtered reduction mixture with a solution of phenanthraquinone in sodium bisulphite.

The *ortho*amidonaphthol derivatives, obtained by reducing azo-compounds containing naphthol sulphonic acids as second components, are unstable, and give characteristic coloured substances on oxidation in the air or on treatment with weak oxidising agents.

The following analysis of Congo red by Witt (*Ber.*, 1886, xix. 1721) illustrates the method by which azo-dyestuffs can be identified by means of the quinoxaline derivative of the second component.

The dyestuff is dissolved in a little water and the solution rendered strongly alkaline with ammonia; zinc dust is then added, upon which the red colour of the solution almost instantly disappears. On cooling, the whole of the benzidine crystallises out, and can be isolated by filtering the solution and extracting the benzidine from the unchanged zinc by treating with alcohol.

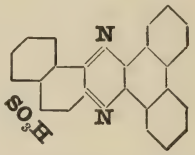
The filtrate, which contains the diamidonaphthalene sulphonic acid, is then acidified with acetic acid, heated to boiling, and then treated quickly with a hot solution of phenanthraquinone.

If a molecular quantity of Congo red (7 grams) has been taken in the original reduction, this phenanthraquinone solution must consist of 4 grams phenanthra-

quinone dissolved in the requisite quantity of sodium bisulphite solution on the water-bath, to which must also be added an excess of sodium acetate.

Almost directly after mixing the solutions crystals begin to appear, and shortly the whole solution becomes solid, owing to the separation of fine lemon-yellow needles. These are filtered and washed with cold water.

This substance, which is the sodium salt of the quinoxaline sulphonic acid of the formula



is best recrystallised by dissolving in hot water, adding an equal volume of alcohol, and then a drop of caustic soda solution. On cooling, the sodium salt separates in the form of fine silky needles.

Concentrated sulphuric acid dissolves this substance, forming a violet solution, which, on dilution with water, becomes a brilliant orange.

The action of concentrated sulphuric acid on the azo-dyestuffs.—Nearly all the azo-dyestuffs yield characteristic colours with concentrated sulphuric acid, which frequently serves as an excellent means of identifying them.

Furthermore, it is sometimes possible by this means to determine the homogeneous character, or otherwise, of any commercial specimen.

For this purpose two or three drops of concentrated sulphuric acid should be placed in a white porcelain dish, and the finely powdered specimen dusted into it. This can be best effected by placing a small quantity of the dyestuff on the end of a spatula and blowing it on to the acid from some little distance away. Notice is then made as to whether each particular particle dissolves with the same or a different colour.

As already mentioned (p. 55) the colour produced by dissolving the azo-dyestuffs in concentrated sulphuric acid depends upon their constitution.

Thus dyestuffs from	give
Amidoazobenzene sulphonic acids + β-naphthol	green.
Amidoazobenzene and homologues + β-naphthol sulphonic acids .	red-violet.
Amidazobenzene sulphonic acids + β-naphthol sulphonic acids . .	blue.

Cp. *Ber.*, 1880, xiii. 1840; 1889, xxii. 634, 2062.

The Titration of Azo-dyestuffs with Titanous Chloride.

(Knecht, *J. Soc. Dyers and Colourists*, 1903, No. 6, vol. xix.)

This method consists in titrating the azo-dyestuff with a solution of titanous chloride, the calculation being based upon the equation

$$TiCl_3 + HCl \rightarrow TiCl_4 + H$$

from which it follows that each azo-group (– N : N –) requires $4TiCl_3$ (or 4Fe) for its complete reduction.

Storing and standardising the titanous chloride solution. — The most convenient strength for general use is a 1 per cent. solution, obtained by diluting the commercial product with water. For this purpose 50 c.c. of the commercial 20 per cent. solution are first mixed with an equal volume of strong hydrochloric acid, and boiled for a few minutes in a flask. The solution is then made up to a litre with distilled water, which has been previously boiled with the

addition of a little hydrochloric acid and a small piece of marble to expel dissolved oxygen.

With a powerful reducing agent like titanous chloride, care must be taken that it is stored and measured in vessels in which it is out of contact with the air, and a simple apparatus for this purpose is that shown in the figure.

Sufficient of the reagent is prepared to completely fill the storage vessel *a*, which is connected with the burette *b*, both storage vessel and burette being kept under constant hydrogen pressure from the small hydrogen generator *d*, where the gas is produced from zinc and dilute sulphuric acid. When liquid is withdrawn from the burette, the pressure is released and hydrogen is at once generated at *d*, so that the interior of the apparatus which is not filled with liquid contains hydrogen at a pressure of about 3 inches.

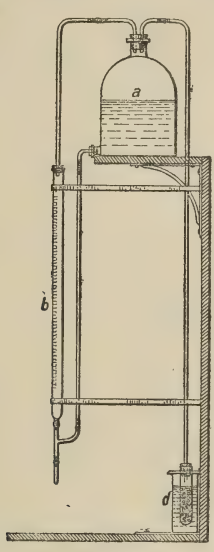


FIG. 11.

If these precautions are taken the solution can be kept unchanged for a considerable period.

Standardising the titanous chloride solution can be effected in the following way:—35 grams of ferrous ammonium sulphate are dissolved in dilute sulphuric acid and made up to 1 litre; 25 c.c. of this solution are now measured into a flask, and weak permanganate solution run in until a pink colour is just perceptible. Into this solution titanous chloride is run, in the cold, until a drop taken out on a glass rod and spotted on sulphocyanide of potash solution no longer shows a red coloration. When two or more titrations agree, the iron value per c.c. of the titanous chloride solution can be easily calculated.

Estimation of azo-compounds.—The estimation of the azo-dyestuff can be accomplished by either of the following methods, depending upon the solubility or otherwise of the compound in dilute mineral acid:—

Soluble.—The titration can be carried out direct, the colouring matter acting as its own indicator. The following example illustrates this method:

Crystal scarlet 6R, $C_{20}H_{12}N_2S_2O_2Na_2 + 7H_2O$ (azo-dyestuff from α-naphthylamine and G salt).—·5 gram of the dyestuff was dissolved in distilled water and the solution made up to 500 c.c. Of this, 100 c.c. were measured out into a conical flask, and, after adding about 10 c.c. concentrated hydrochloric acid, boiled

for about a minute. This amount required 22·6 c.c. of titanous chloride solution for complete decolorisation calculation:—

1 c.c. $TiCl_3$ = 0·0015797 gram Fe
and 502 grams colour require by theory 224 grams Fe,

$$\therefore \frac{0{\cdot}0015797 \times 22{\cdot}6 \times 502}{224} = 0{\cdot}08001 \text{ gram colour}$$

			Calc.
and 1 gram contains 0·8001	→	80·01 per cent.	79·76
Water of crystallisation at 140°	→	19·96 „	20·04
		99·97 „	100·00

In the case of dyestuffs which, like the majority of the benzidine derivatives, are thrown out of solution by hydrochloric acid, the reaction is too slow, and the end point often not sufficiently sharp to admit of exact estimations. In such cases it is best to run in an excess of titanous chloride solution into the boiling solution of the dyestuff, taking the precaution to keep a gentle current of carbonic acid (from a Kipp generator) passing into the flask by a tube which almost touches the surface of the liquid. The reduction will usually be completed in less than two minutes, when the flask is cooled under the tap, without, however, interrupting the current of carbonic acid. When cold, the excess of titanous chloride is estimated by running in an iron-alum solution of known strength (preferably nearly equivalent to that of the titanous chloride solution) until a drop taken out and spotted on sulphocyanide of potash solution just shows a red colour.

By subtracting the number of c.c.'s of the iron-alum solution (or their equivalent in titanous chloride, should the two solutions not be of equal strength) from the total number of c.c.'s of titanous chloride run in, the exact amount of the latter used up in the reduction of the dyestuff is arrived at.

The following example illustrates this method:—

Benzopurpurine 4B, $C_{34}H_{26}N_6S_2O_6K_2 + 4\frac{1}{2}H_2O$ (potassium salt of the azo-dyestuff from tolidine and naphthionic acid).—·5 gram of the dyestuff was dissolved in distilled water, and the solution made up to 500 c.c. Of this, 100 c.c. were measured into a conical flask and heated to boiling; 10 c.c. of concentrated hydrochloric acid and 50 c.c. of titanous chloride solution were then added, carbonic acid being passed into the flask. The contents of the flask were now boiled for about a minute, when complete reduction took place, and, after cooling, the solution required 22·9 c.c. iron-alum solution (equivalent to 21·0 c.c. titanous chloride).

The excess of titanous chloride added was therefore 21·0 c.c., and this, subtracted from 50, gives 29·0 c.c. titanous chloride as having been used for the reduction.

Calculation.—

1 c.c. $TiCl_3$ = 0·001845 gram Fe
and 756 grams colour require by theory 448 grams Fe,

$$\therefore \frac{0{\cdot}001845 \times 29 \times 756}{448} = 0{\cdot}09026 \text{ gram colour,}$$

		Calc.
and 1 gram contains 0·9026 =	90·26 per cent.	90·33 per cent.
Water of crystallisation =	9·63 „	9·67 „
	99·89 „	100·00 „

This method of titrating with titanous chloride has also been applied by its discoverer to the estimation of nitro-compounds, such as nitrobenzene, picric acid, etc., and dyes such as Gallocyanine, Alizarine, etc. (*J. Soc. Dyers*, 1915, xxxi. 241; see also *New Reduction Methods in Volumetric Analysis*), and Salvaterra (*Monatsh.*, 1913, xxxiv. 255) has applied it to both basic and acid dyes.

The fact, first noticed by Sisley (*Bull. Soc. Chim.*, 1901, p. 862), that the azo-compounds contained water of crystallisation when crystallised from their aqueous solutions, has an important bearing upon their estimation, and care should always be taken to estimate the water of crystallisation by heating a weighed quantity to constant weight in an air-bath. (Compare the analyses by Knecht of *Chrysophenine, Brilliant yellow, and Erika* B, *J. Soc. Dyers*, 1905, 5.) Sodium hyposulphite ("hydrosulphite") has also been shown to be a useful reducing agent in this connection (Grandmougin and Havas, *Chem. Zeit.*, 1912, xxxvi. 1167; Siegmund, *Monatsh.*, 1912, xxxiii. 1431).

The separation of the eight coal-tar dyes which are used in the United States for colouring food, namely, Amaranth, Tartrazine, Erythrosine, Naphthol yellow S, Light green SF yellowish, Orange I, Indigo disulphonic acid, and Ponceau 3 R, is described by Estes (*J. Ind. Eng. Chem.*, 1916, viii. 1123).

Methylene blue.

This basic dyestuff can be analysed by Knecht's method, using titanous chloride exactly as described above.

The method of carrying out the assay of commercial Methylene blue is as follows:—One gram of the sample is dissolved in 250 c.c. of water, and 50 c.c. of this are measured into a conical flask, a few drops of hydrochloric acid added, and the contents of the flask gently warmed over the free flame. A current of carbon dioxide is now passed into the flask, and titanous chloride solution run in until the blue colour just disappears.

The calculation of the percentage of dyestuff is made on the assumption that two equivalents of hydrogen are required for its conversion into the leuco-compound, according to the equation

$$C_{16}H_{18}N_3SCl + H_2 = C_{16}H_{20}N_3SCl$$

A determination of moisture must, of course, also be made (*J. Soc. Dyers*, 1905, 9).

Indigo.

The estimation of Indigo can be effected by a number of methods, which, although by no means absolute, yet are sufficiently accurate for practical purposes.

In the first instance, the amount of ash should be determined by igniting a weighed quantity in a platinum crucible until free from carbon.

In natural Indigo the amount of ash varies from 4 to 30 per cent., but no ash should be left on igniting a specimen of the artificial product.

The most usual adulterants of Indigo are starch, resin, Logwood, and Prussian blue.

Starch can be detected by boiling the specimen with water, filtering, and testing the filtrate with iodine solution; the formation of a blue colour indicates the presence of starch in solution.

It can be estimated by treating the finely ground specimen with chlorine water, until completely decolorised, filtering, washing, drying, and finally weighing. It can be removed completely by boiling for thirty minutes with 4 per cent. hydrochloric acid (Frank and Perkin, *J.C.S.I.*, 1912, xxxi. 372).

Resin is extracted by alcohol and can be estimated by this means.

Logwood is soluble in oxalic acid, and can be detected by treating the ground specimen with a solution of oxalic acid, filtering, and testing the filtrate with sodium aluminate solution, which gives a blue precipitate with Logwood solutions.

Prussian blue is converted, on treatment with caustic soda, into sodium ferrocyanide; it is therefore detected by treating the specimen with caustic soda, filtering, and testing for iron in the filtrate.

Indirubine can be entirely removed by boiling pyridine (Bloxam and Perkin, *J.C.S.*, 1910, xcvii. 1465).

Indigo carmine is often adulterated with oxalic acid.

For the estimation of Indigo the various methods may be divided into

I. Reduction.
II. Oxidation.
III. Colorimetric.
IV. Dye-trials.

I. Reduction.—This process consists in reducing the Indigo to Indigo white, which is subsequently oxidised to the blue and weighed.

II. Oxidation depends upon the decomposition of Indigo on oxidation, and consists in titrating a solution of the blue in concentrated sulphuric acid with various oxidising agents.

III. Colorimetric.—A method of this kind is recommended by Houton-Labillardière (*Dingl. pol. J.*, xxvii. 54; xl. 448). It consists in dissolving the Indigo specimen in concentrated sulphuric acid, and diluting this solution with water until the colour assumes the same shade as that of a solution containing a known quantity of Indigo. This method, according to Ullgreen (*Wagner's J.*, 1865, 650), yields unsatisfactory results.

IV. Dye-trials.—This method is recommended by Chevreul and by E. v. Cochenhausen. It is carried out as follows:—

One gram of Indigo is dissolved in 50 grams fuming sulphuric acid and the solution diluted to 1 litre. This is then used for the dyeing of wool or silk, and the dyed material compared with specimens dyed under the same condition with an Indigo of known value.

It is always advisable to confirm the results obtained by one of the previous methods by subjecting the specimen to a dye-trial.

For an account of the numerous methods which have been from time to time snggested for the analysis of both synthetic and natural Indigo, the original literature[1] must be consulted. The method which seems to be least open to objection, and the one which certainly gives the best practical results, is the tetrasulphonate process of Bloxam (*J.C.S.I.*, 1906, xxv. 735).

1. *The separation of Indigotin as potassium indigotintetrasulphonate.*—One gram of the sample, dried previously at 110°, is heated in a water oven for half an hour with 2 or 3 grams of clean sand and 5 c.c. of fuming sulphuric acid (20 per cent. SO_3). After cooling, the mixture is diluted to 500 c.c. with water; 100 c.c. of this solution are placed in a capacious conical beaker and 100 c.c. of a 45 per cent. potassium acetate solution are run in; the contents of the beaker are next heated until complete solution of the precipitate has taken place (a temperature of 90° C. should not be exceeded (Frank and Perkin, *J.C.S.I.*, 1912, xxxi. 372)), and then cooled by placing the beaker in a mixture of ice and water for one hour. The

[1] A detailed account is given in *A Manual of Dyeing*, by Knecht, Rawson, and Löwenthal, 2nd ed., p. 815, and *Technical Methods of Chemical Analysis*, Lunge-Keane, Vol. II. Part ii., p. 1133.

tetrasulphonate separates as a fine-grained, crystalline precipitate, and this is collected on a filter moistened with a solution prepared by adding 5 c.c. of glacial acetic acid to 200 c.c. of 45 per cent. potassium acetate solution, and diluting the mixture with 400 c.c. of water. The precipitate is subsequently washed with this solution at 0° C.

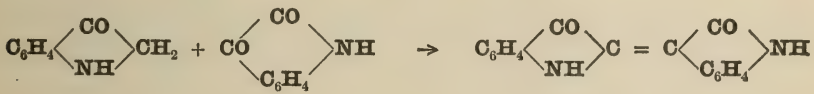
2. *Titration of the precipitate with potassium permanganate or titanium trichloride.*—The precipitate is dissolved off the filter with hot water, and the solution made up to 200 c.c. with water.

Potassium permanganate titration.—20 c.c. of the tetrasulphonate solution are diluted with 80 c.c. of water, 0·5 c.c. of sulphuric acid is added, and a 0·1 per cent. potassium permanganate solution run in until the addition of a drop no longer produces a cloud in the pure yellow liquid. Pure Indigotin would require in these circumstances 9·0 c.c. of permanganate, and percentages are calculated from this standard.

Titanium trichloride titration.—25 c.c. of the tetrasulphonate solution are treated with 1·5 c.c. of a 20 per cent. disodium tartrate solution, and the mixture titrated at a boiling temperature in an atmosphere of carbon dioxide or hydrogen.

Subsequent investigations by Orchardson, Wood, and Bloxam (*J.C.S.I.*, 1907, xxvi. 4) show that the impurities of natural Indigo—Indigo-gluten, Indigo-brown, and Indigo-yellow—are removed by this process, and that the whole of the Indigotin can be obtained as potassium indigotintetrasulphonate when proper precautions are taken. The only impurity which presents any difficulties is Indian yellow (Kæmpherol), for although the sulphonic acid of this substance is not precipitated by the addition of the usual amount of potassium acetate solution, some of it tends to be carried down mechanically. It is therefore necessary to wash the precipitated indigotintetrasulphonate with the isotonic solution of potassium acetate until the yellow colour of the washing gives place to light blue, for which purpose the use of the isotonic solution at the ordinary temperature, instead of ice cold, is recommended.

Gaunt, Thomas, and Bloxam (*J.C.S.I.*, 1907, xxvii. 1174), however, arrive at the conclusion that the only trustworthy method for the analysis of the leaf is the *isatin process*, which depends on the formation of Indirubine from the indoxyl formed by the hydrolysis of the indican contained in the leaf extract and added isatin



in accordance with the v. Baeyer synthesis (see page 181).

The method is carried out as follows :—

Preparation of the leaf extract.—5 grams of dry leaf are placed in a dry glass filter funnel provided with a paper, the base of the funnel being fitted with an indiarubber tube and clip. The clip is closed, the leaf rapidly covered with boiling water and allowed to remain so immersed for about a minute; the clip is then removed, and when the liquid has filtered through, the leaf is washed several times with water at 60° C. To test whether extraction is complete, the last washings are collected separately, and treated with a little 4 per cent. sulphuric acid and 2 per cent. ammonium sulphate, and warmed to 60° C., when there should be no production of blue.

Estimation.—The most suitable volume for estimation is 250 c.c., and the solution is best of such a strength that this volume yields approximately 0·1 gram of Indirubine; for this purpose 0·1 gram of isatin and 15–20 c.c. of pure hydrochloric acid are required.

Air is expelled from the flask by means of a current of carbon dioxide, which is maintained during the whole time of the experiment. The mixture of isatin and plant extract is boiled for 5–10 minutes, and the acid is then run in slowly from a stoppered funnel; the liquid meanwhile is boiled very gently, whilst the gas current is increased to guard against entrance of air. The mixture is boiled for 20–30 minutes, cooled in a current of cold water, the precipitate collected on a weighed filter-paper, washed very thoroughly with 1 per cent. caustic soda solution at 70° C., and then with 4 per cent. acetic acid. It is finally dried in an oven till of constant weight.

Analysis of Naphthol yellow S by Titration with Night blue.

A standard solution of Night blue is prepared by dissolving 10 grams in 50 c.c. of glacial acetic acid and diluting with water to 1 litre.

Solutions of the samples of Naphthol yellow S are prepared so as to contain 1 gram per litre. The operation is carried out as follows:—10 c.c. of Night blue solution are carefully measured into a small flask, and then about 30 c.c. of the solution of yellow run in from a burette; the mixture is well shaken for about a minute and then poured on to a filter. If the filtrate be of a distinct yellow colour, a second experiment is performed in a similar manner with a smaller quantity of the solution of yellow; if the filtrate be blue or *even colourless*, more of the yellow solution is required.

These experiments are repeated with varying quantities of the Naphthol yellow solution until the filtrate possesses a very faint, scarcely perceptible yellow tint. It is best to collect the filtrate in clear Nessler glasses. With a little practice the number of experiments for each sample may be reduced to three or four. The value of the samples under examination will be in inverse proportion to the number of c.c. required to precipitate 10 c.c. of Night blue. For example, if, of two samples, one requires 28 c.c. and the other 35 c.c., their relative value will be as 35 : 28, or expressed centesimally as 100 : 80. If it be desired to express the percentage of pure colouring matter present in the samples, the Night blue solution may be standarised by means of recrystallised Naphthol yellow S, which is the potassium salt of dinitro-α-naphthol sulphonic acid. One gram of *commercial* Night blue precipitates about 0·25 gram of pure dry Naphthol yellow S. It would thus appear that two molecules of Night blue combine with one molecule of Naphthol yellow S to form the insoluble precipitate (Knecht, Rawson, and Löwenthal, *A Manual of Dyeing*).[1]

II. Qualitative Analysis of Dyestuffs.

In powder form the synthetic dyestuffs met with in commerce are sometimes mixtures of two or more compounds which are prepared for the purpose of procuring some certain shade of colour.

It must therefore not be supposed that the various compounds described under technical names in the foregoing pages represent in many cases anything but an approximation to their constitution.

In most instances the formulæ are derived from the patent specifications, and that these do not always represent the true nature of the dyestuff has been pointed out by R. Meyer (*Bull. Soc. Chim.*, 1901, 862), who showed that

[1] Seyewetz (*Sur les Combinaisons des Matières Colorantes basiques avec les Matières Colorantes acides*, Lyons, 1900) has studied the precipitation of acid by basic dyestuffs, and suggests a method of analysis similar to the above. He gives as an example the analysis of Erythrosine by means of a standard solution of Rosaniline hydrochloride.

Chrysophenine possessed a very different constitution from that claimed for it in the patent specification.

Again, the dyestuffs frequently contain impurities either added by design or caused by insufficient washing.

Thus dyestuffs which are precipitated from their solutions by salt contain varying quantities of this substance mixed with them.

Since sodium sulphate is invariably used in the dyeing of wool, many manufacturers add a certain amount of this substance to the finished dyestuff, and the same also applies to other mineral products which are requisite in the application of any particular colouring matter. Mineral impurities of this kind can usually be readily detected.

Sodium chloride can be estimated by extracting the colouring matter with some organic solvent, such as acetone or alcohol, and subsequently determining the chlorine in the residue.

Sodium sulphate nearly always occurs in the azo-dyestuffs. It can be detected by dissolving the colour in water, precipitating by means of salt (free from sulphate), and then testing for sulphate in the filtrate.

Magnesium sulphate is little used; it is tested for in the same way as sodium sulphate.

Alkaline carbonate occurs frequently in dyestuffs of the phthaleïn group. It is estimated by determining the quantity of CO_2 liberated by acids.

Dextrine is often added to the artificial colouring matters. It can be detected by its characteristic smell when the colour is dissolved in water. Generally speaking, it can be isolated by treating the dyestuff with alcohol in which dextrine is insoluble.

The determination of the acid constituent of basic dyestuffs (usually hydrochloric acid, although other acids, such as, for instance, oxalic acids, are used).—The colour is precipitated by ammonia, filtered, and the acid tested for in the filtrate. In the case of colours not precipitated by ammonia, such as Safranine, the acid must be tested for in the dyestuff solution.

The presence of a zinc chloride double salt can be detected by igniting the dyestuff and investigating the residue.

The determination of the basic constituent of acid dyestuffs is carried out in the same way, the acid dyestuff being treated with HCl, filtered, and the base tested for in the filtrate.

The determination of the nature of a dyestuff.—In order to determine whether a dyestuff is a mixture or a homogeneous substance, it is usually sufficient to place a small quantity of it on the end of a spatula, and then to blow it from some distance away on to a sheet of filter-paper moistened with water or alcohol. The particles of dyestuff will settle on the moistened paper, and will immediately begin to dissolve, imparting to the filter-paper its own particular colour.

The homogeneous nature or otherwise of the dyestuff is easily detected by noticing the colours produced by the different particles.

When two colouring matters are present which possess a similar shade, and therefore are not readily detected by this means, it will be frequently found sufficient to blow the dyestuff on to a small quantity of strong sulphuric acid contained in a white porcelain basin, and note any difference in colour produced by the solution of the different particles.

Sometimes the different components of a mixture are very intimately mixed; that is to say, they have either been precipitated together from their solutions, or have been formed by evaporating their solutions to dryness.

In these cases some little difficulty will be experienced in detecting any difference in colour in the spots produced by the above methods, and recourse must then be had to the dye-trial.

This is effected by dyeing a fibre in the solution of the dyestuff for a short time, then removing it and replacing it by another piece of the same fibre, this process being repeated until the dye-bath is completely extracted.

Since it is rare that two dyestuffs have the same affinity for the fibre, the presence of a mixture will be clearly noticeable on comparing the different dyeings (see also p. 377).

In the following tables are given the principal behaviour of typical dyestuffs towards reagents, one or two members of each group being taken and their reactions described.

By this means a certain idea of the reactions of other members of the same group can be derived, although tests of this kind are by no means absolute, and can only be taken as indicating the possible nature of a compound.

The tests have been applied to the pure dyestuffs, and the commercial product should be as far as possible freed from impurities before being treated with the reagents.

In many cases, by selecting suitable reactions, it may be found possible to separate the constituents of a mixture, and to isolate them in such a manner that each can be identified with certainty. For investigations of this kind, however, it is impossible to give rules which are generally applicable, and much practice and manipulative skill are required in order to obtain accurate results.

If the colouring matter to be examined is in solid or powder form, it is dissolved in a thousand times its weight of water; in the case of paste colours a larger quantity is taken, according to the percentage of dry substance they contain. If the colouring matter is soluble, either entirely or nearly so, the solution is filtered, so that in the event of any turbidity or precipitation occurring during examination there need be no doubt upon the point. If, however, the colouring matter is sparingly soluble, or altogether insoluble, the tests are made with a mixture of the finely divided colouring matter held in suspension in water (1 : 1000). Only when tests are made to determine the solubility of the colouring matter in alcohol, ether, and benzene, or to study its behaviour with concentrated sulphuric acid, is it necessary to use it in the dry condition.

When making these solubility tests about ·1 gram of the colouring matter is added to 20 c.c. of the necessary reagent; the mixture is then well shaken, boiled, and filtered. When concentrated sulphuric acid is used it is also desirable not to take too much colouring matter, so that the colour of the solution may not be too dark; a portion of the solution is then poured into a test-tube containing cold water and the effect noted.

With respect to the reactions with other acids, also with alkalies and salts, equal amounts of colour solution and the reagent are mixed together in a test-tube; one-half the mixture is allowed to stand in the cold, and if precipitation takes place it is filtered; the remainder is heated to boiling, note being taken of any changes which occur.

For reducing with zinc dust in conjunction with acids or alkalies, 20 c.c. of the colour solution are mixed with about 5 grams of zinc dust, then about 20 c.c. of acid or alkali are added, and the whole is well shaken, then boiled till decolorised, and at once filtered, after which one must observe whether or not the filtrate becomes coloured on exposure to the air.

This can be effected by spotting a piece of filter-paper with the solution and allowing it to slowly dry in the air.

Since the common salt which accompanies dyestuffs which have been recrystallised from salt solutions is extremely difficult to remove by recrystallisa-

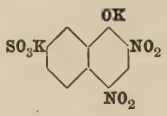
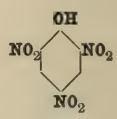
tion, a small quantity of hydrochloric acid gas will frequently be given off in testing with concentrated sulphuric acid.

This is usually the case with the soluble azo-compounds.

Reagents.

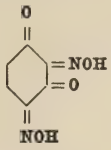
Water,	Distilled.
Alcohol,	Absolute.
Ether,	Chemically pure.
Benzene,	,,
Sulphuric acid,	Concentrated.
Sulphuric acid (dilute),	100 grams concentrated in 1 litre water.
Hydrochloric acid (dilute),	100 c.c. concentrated acid (sp. gr. 1·16) diluted to 1 litre.
Nitric acid,	100 c.c. pure nitric acid diluted to 1 litre.
Sodium hydrate,	100 c.c. sodium hydrate solution (sp. gr. 1·3) diluted to 1 litre.
Ammonia,	Commercial ammonia (sp. gr. ·951).
Sodium carbonate,	100 grams (cryst.) in 1 litre of water.
,, acetate,	100 grams ,, ,, ,, ,,
Tannin solution,	100 grams tannic acid dissolved in 500 c.c. of water and mixed with 100 grams sodium acetate in 500 c.c. of water.
Alum,	50 grams (cryst.) in 1 litre of water.
Potassium bichromate,	50 grams ,, ,, ,, ,,
Ferric chloride,	100 grams ,, ,, ,, ,,
Stannous chloride,	100 grams ,, ,, ,, ,,
Calcium hypochlorite,	1½° Tw. (sp. gr. 1·007), freshly prepared.
Acetic acid,	12° Tw. (sp. gr. 1·06).

The Nitro-dyestuffs.

Colouring matter, .	*Naphthol yellow* S.[1] 	*Picric acid.* 
Description, . .	Bright yellow powder.	Yellow crystals.
Solubility in Water, . .	Readily soluble.	Readily soluble.
Solubility in Alcohol, . .	Somewhat soluble.	Readily soluble.
Solubility in Ether, . .	Insoluble.	Readily soluble.
Solubility in Benzene, . .	Insoluble.	Readily soluble.
Heating on platinum foil,	Explodes, leaving residue of potassium carbonate.	Explodes with a luminous flame.
Conc. H_2SO_4, . .	Dissolves with yellow-green colour; on dilution with water, becomes pale yellow; on heating, conc. solution becomes olive-brown.	Insoluble.
Dil. H_2SO_4, . .	Becomes pale yellow.	Unchanged.
Sodium hydrate, .	Unchanged.	Reddish-yellow solution of sodium salt.
Ammonia, . .	Unchanged.	Reddish-yellow solution of ammonium salt.
Tannin reagent, .	Unchanged.	Unchanged.
Alum, . . .	Unchanged.	Unchanged.
Potassium bichromate,	Unchanged.	Unchanged.
Stannous chloride, .	Is not decolorised.	On boiling, becomes dirty yellow; on standing, decolorised.
Zinc dust and ammonia,	Reduced; in the filtrate yellow colour returns.	Quickly decolorised; filtrate dirty red.
Zinc dust and acetic acid,	Reduced with difficulty; filtrate and filter-paper become coloured orange-red.	Quickly decolorised; filtrate olive, edges of filter-paper blue.

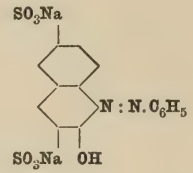
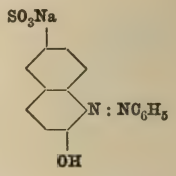
[1] See *Night blue titration* (p. 342).

The Nitroso-dyestuffs.

Colouring matter, ...	*Resorcin green, Solid green* O. 
Description, ...	Drab-coloured stiff paste (50 per cent.).
Solubility in: Water, ...	Soluble on boiling; brown solution.
Solubility in: Alcohol, ...	Soluble; yellowish solution.
Solubility in: Ether, ...	Insoluble.
Solubility in: Benzene, ...	Insoluble.
Heating on platinum foil, . .	Burns away quickly and regularly, leaving no ash.
Conc. H_2SO_4, ...	Dissolves with a deep brown colour; on dilution with water, partial precipitation; on heating, conc. solution gives off gas and becomes redder.
Dil. H_2SO_4, ...	On heating, a clear pale yellow solution, not extracted by ether.
Sodium hydrate, ...	Yellow solution, not extracted by ether.
Ammonia, ...	Yellow solution.
Tannin reagent, ...	...
Alum, ...	On heating, a pale yellow solution.
Potassium bichromate, . . .	Dissolves on heating.
Stannous chloride, ...	White precipitate; filtrate on heating colourless.
Zinc dust and ammonia, . . .	Easily reduced; filtrate and edges of the filter-paper become violet-blue.
Zinc dust and acetic acid, . .	...

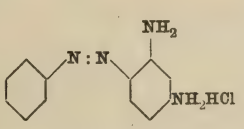
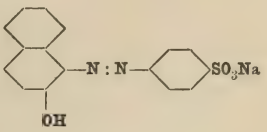
The Azo-dyestuffs.

Monazo.

Colouring matter, .	*Orange* G.	*Ponceau* 4GB.
		
Description, . .	Yellow-scarlet powder.	Yellow-scarlet powder.
Solubility in Water, . .	Readily soluble ; orange.	Fairly soluble ; orange.
Solubility in Alcohol, . .	Readily soluble ; orange.	Fairly soluble ; orange.
Solubility in Ether, . .	Insoluble.	Soluble in traces.
Solubility in Benzene, . .	Insoluble.	Soluble in traces.
Heating on platinum foil,	Chars and finally burns away, leaving white ash.	At first emits a white vapour, then burns with a luminous flame and puffs up strongly ; finally chars and leaves white fusible residue.
Conc. H_2SO_4, . .	Dissolves with an orange colour ; on dilution, reddish-yellow ; on heating, conc. solution becomes red.	Dissolves with an orange colour ; on dilution, becomes reddish-yellow ; with only a little water, a pale dirty red precipitate ; on heating, the conc. solution becomes darker, then ruby-red, and finally black.
Dil. H_2SO_4, . .	Unchanged.	Unchanged.
Sodium hydrate, .	Red solution.	Solution becomes slightly redder.
Ammonia, . .	Red-yellow solution.	Solution becomes slightly redder.
Tannin reagent, .	Unchanged.	Unchanged.
Alum, . . .	Unchanged.	Unchanged.
Potassium bichromate,	Unchanged.	Unchanged.
Stannous chloride, .	Orange ; decolorised on long boiling.	Orange-yellow precipitate ; on boiling, decolorised fairly rapidly.
Zinc dust and ammonia.	Quickly reduced ; filtrate pure yellow.	Rapidly decolorised ; filtrate pale greenish-yellow.
Zinc dust and acetic acid,	Somewhat quickly reduced ; filtrate colourless.	Quickly reduced ; filtrate colourless.

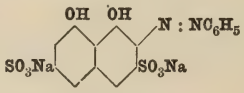
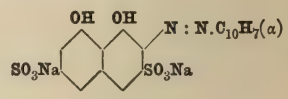
The Azo-dyestuffs—*continued.*

Monazo—continued.

Colouring matter, .	*Chrysoïdine.* 	*Orange II.* 
Description, .	Black crystals with metallic lustre.	Yellow-scarlet powder.
Solubility in Water, . .	Very soluble.	Readily soluble; orange.
Solubility in Alcohol, . .	Very soluble.	Readily soluble; orange.
Solubility in Ether, . .	Soluble in traces; pale yellow.	Insoluble.
Solubility in Benzene, . .	Soluble in traces.	Insoluble.
Heating on platinum foil,	Melts; gives off a brown, aromatic vapour, and then burns with a bright flame; finally chars and leaves no ash.	Burns with luminous flame; puffs up to form a voluminous black mass, which finally burns away, leaving white ash.
Conc. H_2SO_4, . .	Dissolves with evolution of HCl, solution yellow; on dilution, becomes orange; conc. solution, on heating, becomes dark olive.	Dissolves with a ruby-red colour; on dilution, orange-yellow; on heating, conc. solution becomes more yellowish, finally brownish-black.
Dil. H_2SO_4, . .	Unchanged.	Unchanged.
Sodium hydrate, .	Orange-yellow precipitate; extracted by ether.	Solution becomes redder; remains clear.
Ammonia, . .	Partial orange-yellow precipitate; soluble in excess, extracted by ether.	Solution somewhat redder; remains clear.
Tannin reagent, .	Partial orange-brown precipitate; soluble on heating.	Unchanged.
Alum, . . .	Unchanged.	In the cold, partial precipitation, orange-red; on heating, redissolves.
Potassium bichromate,	Quantitative brick-red precipitate; on heating, becomes dark brown and resinous.	Unchanged.
Stannous chloride, .	In the cold, unchanged; on heating, turbid brown-yellow.	Orange-yellow precipitate; on boiling rapidly, decolorised.
Zinc dust and ammonia,	Rapidly decolorised; filtrate and edge of the filter-paper yellowish.	Rapidly decolorised; filtrate pale yellow.
Zinc dust and acetic acid,	Rapidly decolorised; filtrate almost colourless.	Quickly decolorised; filtrate and edges of the filter-paper pale pink.

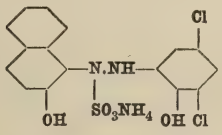
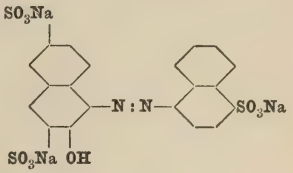
The Azo-dyestuffs—*continued.*

Monazo—continued.

Colouring matter, .	*Chromotrope* 2R. 	*Chromotrope* 10B. 
Description, . .	Brown-red powder.	Brown powder.
Solubility in: Water, . .	Red solution.	Magenta-red solution.
Solubility in: Alcohol, . .	Red solution.	Magenta-red solution.
Solubility in: Ether, . .	Insoluble.	Insoluble.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	Glows without emitting vapour, leaving white ash.	Glows and emits vapour; melts partially, leaving a little fused ash.
Conc. H_2SO_4, . .	Dissolves with effervescence, solution magenta-red; on dilution, red; on heating, conc. solution brownish-red.	Dissolves with effervescence, solution blue; on dilution, violet; on heating, conc. solution brown-red.
Dil. H_2SO_4, . .	Unchanged.	Unchanged.
Sodium hydrate, .	Unchanged.	Unchanged.
Ammonia, . .	Unchanged.	Unchanged.
Tannin reagent, .	Unchanged.	Unchanged.
Alum, . . .	Unchanged.	In the cold, complete precipitation, dark violet; on boiling, decolorised.
Potassium bichromate,	Somewhat darker.	...
Stannous chloride, .	In the cold, partial precipitation, rose-pink; on boiling, decolorised.	Unchanged.
Zinc dust and ammonia,	Decolorised; filtrate becomes yellow.	Decolorised; filtrate becomes reddish-yellow.
Zinc dust and acetic acid,	Decolorised; filtrate colourless.	Decolorised; filtrate colourless.

The Azo-dyestuffs—*continued.*

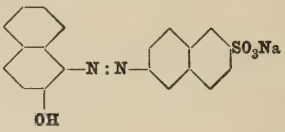
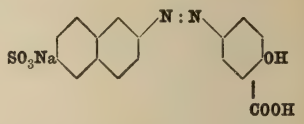
Monazo—continued.

Colouring matter, .	*Azarine* S.[1] 	*Fast red* D—*Amaranth.* 
Description, . .	Brown-yellow paste.	Dark brown powder.
Solubility in Water, . .	Fairly soluble ; yellow.	Readily soluble.
Solubility in Alcohol, . .	Readily soluble ; yellow.	Sparingly soluble.
Solubility in Ether, . .	Somewhat soluble ; yellow.	Insoluble.
Solubility in Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	After the evaporation of the water, the residue emits a quantity of reddish vapour, ignites, chars, and finally burns away, leaving no ash.	Very soon ceases to glow and melts, forming a yellowish-red glowing mass, eventually leaving a white ash, which is readily fusible.
Conc. H_2SO_4, .	Dissolves with evolution of SO_2, solution deep violet-red ; on dilution, quantitatively precipitated, brown-red ; on heating, conc. solution becomes dirty brown.	Dissolves, forming blue-violet solution ; on dilution with water, bluish-red solution ; on heating, the conc. solution becomes violet brown.
Dil. H_2SO_4, . .	In the cold, partial precipitation ; on heating, clear solution, extracted with ether, yellow.	Unchanged.
Sodium hydrate, .	Violet precipitate, pale red filtrate ; extracted with ether, blue, the aqueous solution being a dirty reddish colour.	Dark red solution.
Ammonia, . .	Same as with sodium hydrate.	Darker solution.
Tannin reagent, .	...	Unchanged.
Alum, ...	On heating, yellow solution.	Unchanged.
Potassium bichromate,	On heating, brown turbidity.	Unchanged.
Stannous chloride, .	On heating, partial precipitation; yellow.	...
Zinc dust and ammonia,	Easily reduced ; filtrate becomes pale yellow.	Quickly reduced ; filtrate pale greenish-yellow.
Zinc dust and acetic acid,	...	Reduced with some difficulty ; filtrate pale pink.

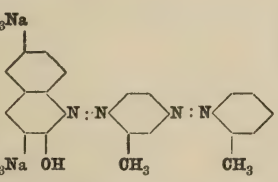
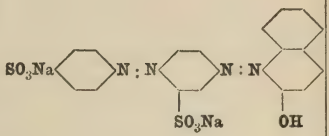
[1] Formed by the action of ammonium bisulphite on the azo-compound.

The Azo-dyestuffs—*continued.*

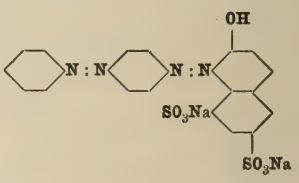
Monazo—continued.

Colouring matter, .	*Double brilliant scarlet—Scarlet for silk.* 	*Mordant yellow* O. 
Description, . .	Brick-red powder.	Red-yellow powder.
Solubility in Water, . .	Readily soluble.	Soluble in water ; yellow.
Solubility in Alcohol, . .	Soluble.	Not readily soluble.
Solubility in Ether, . .	Soluble in slight traces.	Soluble in traces.
Solubility in Benzene, . .	Soluble in slight traces.	Insoluble.
Heating on platinum foil,	Puffs up, burns, chars, and finally leaves a fusible white ash.	Puffs up strongly and then melts, leaving a little ash.
Conc. H_2SO_4, . .	Dissolves, solution magenta-red ; on dilution, a red-brown precipitate ; on heating, conc. solution becomes dirty violet-red.	Brick red with evolution of gas ; on dilution, yellow with partial separation of a yellow precipitate.
Dil. H_2SO_4, . .	In the cold, a yellowish-red precipitate, which, on heating, dissolves, forming pale reddish-yellow solution.	...
Sodium hydrate, .	Unchanged.	Orange liquid.
Ammonia, . .	Unchanged.	Orange liquid.
Tannin reagent, .	Unchanged.	Acquires a darker colour.
Alum, . . .	In the cold, a yellowish-red flocculent precipitate, which, on heating, redissolves.	Unchanged.
Potassium bichromate,	Unchanged.	Unchanged.
Stannous chloride, .	Yellowish-red precipitate ; on long boiling, decolorised.	Completely precipitated ; yellow.
Zinc dust and ammonia,	Quickly reduced ; filtrate pale yellow.	In the cold, not decolorised.
Zinc dust and acetic acid,	Somewhat quickly reduced ; filtrate colourless.	Completely decolorised on boiling.

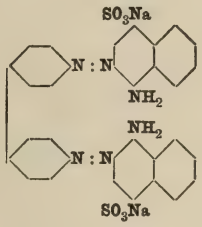
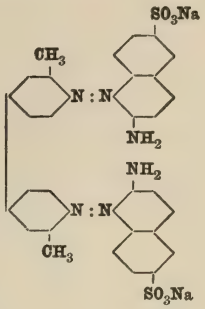
Disazo-dyestuffs.

Colouring matter, .	*Cloth red* O. 	*Biebrich scarlet.* 
Description, . .	Dark greenish-brown powder.	Brick-red powder.
Solubility in: Water, . .	Readily soluble.	Turbid solution.
Solubility in: Alcohol, . .	Sparingly soluble.	Fairly soluble.
Solubility in: Ether, . .	Insoluble.	Soluble in traces.
Solubility in: Benzene, . .	Insoluble.	Soluble in traces.
Heating on platinum foil,	Emits a large quantity of yellow vapour, burns with a strongly luminous flame, chars, and finally leaves fused white ash.	Becomes darker, then puffs up strongly, forming grey mass, which finally leaves a white fusible ash.
Conc. H_2SO_4, . .	Dissolves, forming dark-blue solution; on dilution, bluish-red; on heating, conc. solution becomes yellowish-brown.	Dissolves with a Malachite green colour; on dilution, becomes blue, then violet, and finally red; on heating, the conc. solution becomes blue, then dirty blue, and finally yellowish-brown.
Dil. H_2SO_4, . .	Unchanged.	Unchanged.
Sodium hydrate, .	Partial precipitation, bluish-red; on heating, redissolves.	Becomes darker red-violet; partial precipitation, rusty-brown; filtrate red-violet.
Ammonia, . .	Same as with sodium hydrate.	Solution becomes darker.
Tannin reagent, .	Unchanged.	Unchanged.
Alum, . . .	Partial precipitation, bluish-red; on heating, partly soluble.	In the cold, a yellowish-red flocculent precipitate, which, on heating, partly dissolves.
Potassium bichromate,	In the cold, quantitative precipitation, carmine-red; on heating, becomes hard.	In the cold, partial precipitation, yellowish-red; on heating, redissolves.
Stannous chloride, .	Dirty bluish-red; decolorised on long standing.	Yellowish-red precipitate; on boiling, red; decolorised on long boiling.
Zinc dust and ammonia,	Quickly reduced; filtrate and edges of the filter-paper yellow.	Quickly reduced; filtrate pure yellow.
Zinc dust and acetic acid,	Reduced with some difficulty; filtrate colourless.	Somewhat rapidly reduced; filtrate pale pink.

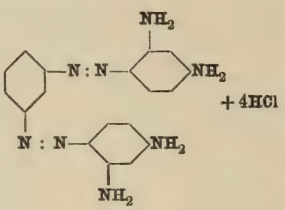
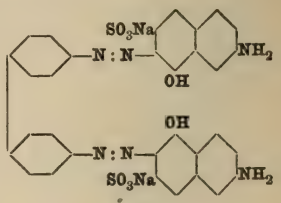
Disazo-dyestuffs—*continued.*

Colouring matter, ...	*Brilliant croceine.* 
Description, ...	Brick-red powder.
Solubility in: Water, ...	Readily soluble.
Solubility in: Alcohol, ...	Fairly soluble.
Solubility in: Ether, ...	Insoluble.
Solubility in: Benzene, ...	Insoluble.
Heating on platinum foil, . .	Puffs up and quickly burns away, leaving small quantity of fusible white ash.
Conc. H_2SO_4, ...	Dissolves, forming red-violet solution; on dilution with water, partly precipitated, black; filtrate pale red; on heating, conc. solution becomes blackish-brown.
Dil. H_2SO_4, ...	Unchanged.
Sodium hydrate, ...	Dark dirty red solution.
Ammonia, ...	Dark dirty red solution.
Tannin reagent, ...	Unchanged.
Alum, ...	Unchanged.
Potassium bichromate, . . .	Unchanged.
Stannous chloride, ...	In the cold, partially precipitated; on heating, decolorised.
Zinc dust and ammonia, . . .	Rapidly decolorised; filtrate pure yellow.
Zinc dust and acetic acid, . .	Rapidly decolorised; filtrate colourless.

Dyestuffs from Tetrazo-salts.

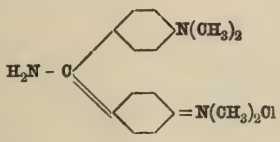
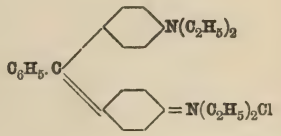
Colouring matter, .	*Congo red.* 	*Benzopurpurine* B. 
Description, . .	Red-brown powder.	Red-brown powder.
Solubility in: Water, . .	Readily soluble.	Readily soluble; yellowish-red.
Solubility in: Alcohol, . .	Sparingly soluble.	Sparingly soluble.
Solubility in: Ether, . .	Insoluble.	Insoluble.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	Burns slowly, chars, and finally leaves a fusible ash.	Burns slowly, chars, and finally leaves a white fusible ash.
Conc. H_2SO_4, .	Dissolves, forming blue solution; on dilution, blue precipitate.	Dissolves, forming blue solution; diluted, dark brown flocculent precipitate.
Dil. H_2SO_4, . .	Blue precipitate.	Brown precipitate.
Sodium hydrate, .	Reddish-brown precipitate, soluble in water.	Unchanged.
Ammonia, . . .	The same as sodium hydrate.	Unchanged.
Tannin reagent, .	Unchanged.	Unchanged.
Alum, . . .	Unchanged.	Unchanged.
Potassium bichromate,	Unchanged.	Unchanged.
Stannous chloride,	Slowly decolorised.	Decolorised on boiling.
Zinc dust and ammonia,	Readily reduced; filtrate colourless.	Readily reduced; filtrate colourless.
Zinc dust and acetic acid,	Readily reduced; filtrate colourless.	Readily reduced; filtrate colourless.

Dyestuffs from Tetrazo-salts—*continued.*

Colouring matter, .	*Bismarck brown.* 	*Diamine black* RO. 
Description, . .	Dark brown powder.	Black powder.
Solubility in: Water, . .	Readily soluble.	Violet-black solution.
Solubility in: Alcohol, . .	Readily soluble.	Sparingly soluble.
Solubility in: Ether, . .	Insoluble.	Insoluble.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	Gives off white vapour, chars and burns away, leaving no ash.	Burns with luminous flame, chars and leaves white fusible residue.
Conc. H_2SO_4, .	Dissolves, with evolution of HCl, to dark brown solution; on dilution, dark yellow-brown with partial precipitation; conc. solution, on heating, becomes black-olive.	Dissolves, forming blue solution; on dilution, reddish-blue precipitate.
Dil. H_2SO_4, . .	In the cold, partial dark precipitate; dissolves to reddish-yellow solution on warming.	Reddish-blue precipitate
Sodium hydrate, .	Partial yellow-brown precipitate, extracted with ether.	Violet solution.
Ammonia, . .	Same as with sodium hydrate.	Violet solution.
Tannin reagent, .	Partial red-brown precipitate; dissolves on heating.	Unchanged.
Alum, . . .	Partial brown precipitate; dissolves on heating.	Unchanged.
Potassium bichromate,	Quantitative dark orange-brown precipitate; on heating, becomes black.	Unchanged.
Stannous chloride, .	Partial orange-brown precipitate; on heating, rapidly decolorised.	Decolorised on boiling.
Zinc dust and ammonia,	Rapidly decolorised; filtrate and edge of filter-paper slightly orange.	Rapidly reduced; filtrate becomes blue on exposure to the air.
Zinc dust and acetic acid,	Rapidly decolorised; filtrate a dirty reddish colour.	Readily reduced; filtrate becomes blue on exposure to the air.

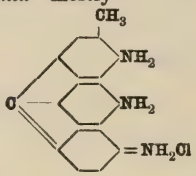
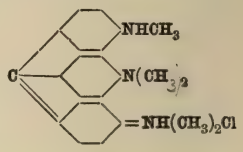
Di- and Triphenylmethane Dyestuffs.

Basic.

Colouring matter, .	*Auramine* O. 	*Brilliant green.* 
Description, . .	Yellow powder.	Green crystalline plates with metallic lustre.
Solubility in: Water, . .	Very soluble; yellow.	Readily soluble.
Solubility in: Alcohol, . .	Very soluble; yellow.	Readily soluble.
Solubility in: Ether, . .	Insoluble.	Soluble in traces.
Solubility in: Benzene, . .	Insoluble.	Soluble in traces.
Heating on platinum foil,	Becomes red-orange, yellow vapour is given off, finally chars and burns away, leaving no ash.	Melts and burns with a smoky flame; the carbon burns away, leaving a little ash.
Conc. H_2SO_4, . .	Dissolves, with evolution of HCl, to colourless solution; on dilution, becomes yellow; conc. solution, on heating, becomes brown-yellow.	Dissolves, giving dark yellow solution; diluted, brownish-yellow; on heating, conc. solution becomes darker.
Dil. H_2SO_4, . .	Unchanged; decolorised on boiling.	Red-brown solution.
Sodium hydrate, .	White precipitate; extracted on shaking by ether.	Dirty pale green precipitate, quantitative; on heating, colourless; extracted by ether.
Ammonia, . .	Same as with sodium hydrate.	The solution becomes milk-white turbid; extracted by ether.
Tannin reagent, .	Almost completely precipitated, yellow; becomes brown and resinous on boiling.	In the cold, almost quantitative precipitate; on heating, somewhat soluble.
Alum, . . .	Unchanged.	Unchanged.
Potassium bichromate,	Quantitative yellow precipitate, which becomes resinous on heating.	Almost quantitative dark green precipitate; on heating, partly soluble; the liquid becomes covered with a coppery iridescent film.
Stannous chloride, .	Unchanged.	In the cold, quantitative green precipitate; on heating, mostly dissolved; filtrate dark green.
Zinc dust and ammonia,	Filtrate colourless; colour does not reappear; on standing, precipitate on filter becomes yellowish.	Filtrate colourless.
Zinc dust and acetic acid,	Becomes blue on reduction.	Reduced with great difficulty; filtrate colourless.

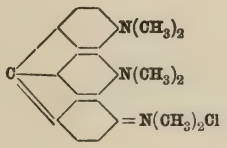
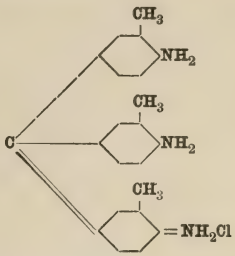
Di- and Triphenylmethane Dyestuffs—*continued.*

Basic—continued.

Colouring matter, .	*Magenta*—mostly 	*Methyl violet* B. 
Description, . .	Dark green crystals, metallic lustre.	Olive-green crystalline powder.
Solubility in Water, .	Readily soluble; purple-red.	Readily soluble; violet.
Solubility in Alcohol, . .	Readily soluble.	Readily soluble; violet.
Solubility in Ether, . .	Soluble in traces; crystals become blue.	Soluble in traces.
Solubility in Benzene, . .	Insoluble; crystals become blue.	In the cold, not very soluble; on heating, moderately soluble.
Heating on platinum foil,	Gives off red vapour, then melts and burns with a smoky flame, leaves no ash.	Emits white vapour, melts and ignites, leaving no ash.
Conc. H_2SO_4, . .	Dissolves with evolution of **HCl**, solution dark brown-yellow; diluted with water, becomes yellowish-red, then yellow, and finally almost colourless; conc. solution, on heating, becomes dark olive-brown.	Dissolves with evolution of **HCl**, solution orange; diluted with water, orange-brown, brown-olive, olive-green, blue-green; on heating, conc. solution becomes brown.
Dil. H_2SO_4, . .	Solution first yellowish-red, then yellow, finally almost colourless; on heating, red colour returns.	Deep red-brown solution; on standing, green.
Sodium hydrate, .	Quantitative red-brown precipitate, extracted by ether.	Quantitative violet-brown precipitate, extracted by ether.
Ammonia, . .	With excess, colourless solution; a slight addition causes turbidity.	Becomes paler and redder; quantitative dirty pale greyish-red precipitate, extracted by ether.
Tannin reagent, .	In the cold, almost quantitative precipitate; on heating, it becomes resinous and partially dissolves.	Quantitative violet precipitate; on heating, filtrate becomes slightly red.
Alum, . . .	In the cold, partial red precipitate; dissolves on heating.	Unchanged.
Potassium bichromate,	Quantitative red-brown precipitate; on heating, becomes resinous.	Quantitative black-violet precipitate; mostly soluble on heating, partly resinous.
Stannous chloride, .	In the cold, partial precipitation; on heating, dissolves with separation of basic stannous chloride.	Almost quantitative violet precipitate; on heating, indigo blue, partly soluble; filtrate azure-blue with green fluorescence.
Zinc dust and ammonia,	Filtrate colourless; edge of filter-paper red.	Filtrate colourless.
Zinc dust and acetic acid,	Reduced with some difficulty; filtrate colourless; on boiling, pale pink.	Reduced with some difficulty; filtrate colourless; the violet colour very slowly restored.

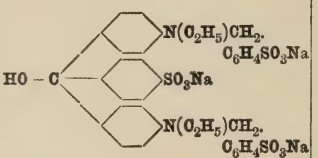
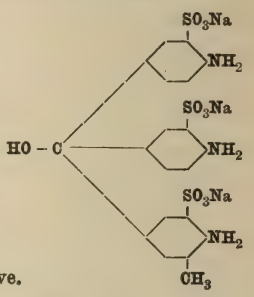
Di- and Triphenylmethane Dyestuffs—*continued.*

Basic—continued.

Colouring matter, .	*Crystal violet.* 	*New magenta.* 
Description, .	Yellow-green crystals with metallic lustre.	Green powder with metallic lustre.
Solubility in Water, . .	Readily soluble; violet.	Magenta-red solution.
Solubility in Alcohol, . .	Readily soluble.	Magenta-red solution.
Solubility in Ether, . .	Almost insoluble.	Soluble in traces.
Solubility in Benzene, . .	Somewhat soluble; the crystals become blue.	Insoluble.
Heating on platinum foil,	The crystals melt and burn with a smoky flame, then char, and finally burn away, leaving no ash.	Chars and leaves no ash.
Conc. H_2SO_4, . .	Dissolves with evolution of **HCl**, solution orange-yellow; diluted with water, olive-green, yellow-green, yellow; on heating, conc. solution becomes dark brown.	Orange-yellow solution, evolution of **HCl**; diluted, yellow; heated, brown-olive; on standing, red-brown flocculent precipitate.
Dil. H_2SO_4, . .	Olive-green solution; on heating, emerald green.	Cold, solution yellow-brown; hot, ruby-red.
Sodium hydrate, .	Blue-violet quantitative precipitate, extracted by ether.	Cold, complete precipitation; red hot, yellow-brown precipitate; filtrate colourless.
Ammonia, . .	The solution becomes milky, eventually milky-white.	Solution pale yellowish-red.
Tannin reagent, .	In the cold, and on heating, quantitative precipitate.	Completely precipitated, brown-red.
Alum, . . .	Unchanged.	Cold, slight brown-red turbidity; hot, clear magenta-red solution.
Potassium bichromate,	Quantitative violet-black precipitate with metallic lustre; on heating, partly soluble (resinous).	Cold, completely precipitated, brown-red; hot, almost clear orange-red.
Stannous chloride, .	In the cold, quantitative violet precipitate; on heating, partly soluble.	Cold, partial violet-red precipitation, soluble on boiling.
Zinc dust and ammonia, .	Filtrate colourless; edges of filter-paper lilac.	Rapidly decolorised on boiling; filtrate colourless.
Zinc dust and acetic acid,	Reduced with difficulty; filtrate becomes pale blue; edges of the filter-paper pale blue-violet.	Easily reduced; filtrate colourless.

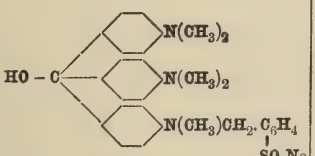
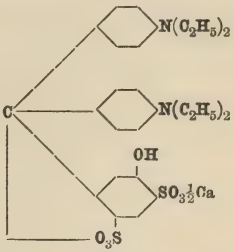
Di- and Triphenylmethane Dyestuffs—*continued.*

Acid.

Colouring matter, .	*Acid green.* 	*Acid magenta*—mostly 
Description, . .	Dark green powder.	Olive.
Solubility in: Water, . .	Readily soluble ; green.	Readily soluble ; magenta-red.
Solubility in: Alcohol, .	Slightly soluble.	Readily soluble.
Solubility in: Ether, . .	Insoluble.	Insoluble.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	Burns away and leaves white fusible ash.	Cakes together, burns away, and finally leaves a white fused ash.
Conc. H_2SO_4, . .	Dissolves, forming dark orange solution ; on dilution, becomes olive, then green ; on heating, conc. solution becomes dark olive-brown.	Dissolves, forming dark orange solution ; diluted, carmine-red ; on heating, conc. solution becomes olive-brown.
Dil. H_2SO_4, . .	On standing, colour becomes paler.	Unchanged.
Sodium hydrate, .	Becomes colourless.	Colourless solution.
Ammonia, . .	Becomes colourless.	Colourless solution.
Tannin reagent, .	Unchanged.	Unchanged.
Alum, . . .	Unchanged.	Unchanged.
Potassium bichromate,	Unchanged.	Unchanged.
Stannous chloride, .	Unchanged.	Unchanged.
Zinc dust and ammonia,	Readily reduced ; filtrate colourless ; on addition of acetic acid, becomes green.	Filtrate colourless ; on addition of acetic acid, colour returns.
Zinc dust and acetic acid,	Reduced with difficulty ; filtrate pale green.	Reduced with difficulty ; filtrate pink.

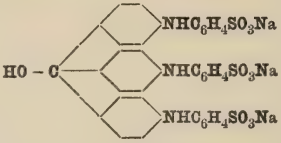
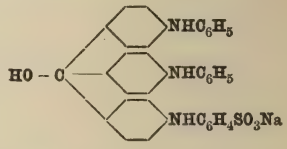
Di- and Triphenylmethane Dyestuffs—*continued.*

Acid—continued.

	Acid violet N.	*Patent blue* V.
Colouring matter, .		
Description, . .	Red-violet powder.	Dark blue crystalline powder.
Solubility in: Water, . .	Dissolves with some difficulty; violet solution.	Readily soluble; greenish-blue.
Solubility in: Alcohol, .	Somewhat readily soluble; violet solution.	Somewhat soluble.
Solubility in: Ether, . .	Insoluble.	Insoluble.
Solubility in: Benzene, . .	Soluble in traces.	Almost insoluble.
Heating on platinum foil,	Emits white vapour, ignites, and leaves fusible white ash.	Emits white vapour, and then burns rapidly, leaving infusible ash.
Conc. H_2SO_4, .	Dissolves, forming brown-orange solution: on dilution, dirty green; with much water, blue.	Dissolves with some difficulty; solution, olive-yellow; on dilution, yellow; on heating, conc. solution becomes darker.
Dil. H_2SO_4, . .	Dirty green solution.	Olive-green solution.
Sodium hydrate, .	On heating, decolorised, and a white flocculent precipitate is formed.	Solution becomes bluer; on heating, blue and then violet.
Ammonia, . .	On standing, solution becomes colourless.	Same as with sodium hydrate.
Tannin reagent, .	Strong fluorescence, partial precipitation in the cold.	Unchanged.
Alum, . . .	Partial precipitation, violet; on heating, becomes resinous and acquires coppery lustre.	Blue-green solution.
Potassium bichromate,	Unchanged.	...
Stannous chloride,	Almost quantitative violet precipitate; filtrate pale blue.	Partial precipitation, yellow-green.
Zinc dust and ammonia,	Easily reduced; the filtrate colourless.	Easily reduced; filtrate colourless.
Zinc dust and acetic acid,	Easily reduced; the violet colour is gradually restored in the filtrate.	Easily reduced; filtrate colourless; on boiling, pale-green.

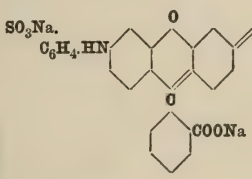
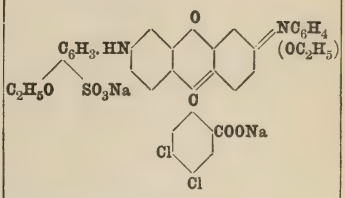
Di- and Triphenylmethane Dyestuffs—*continued.*

Acid—continued.

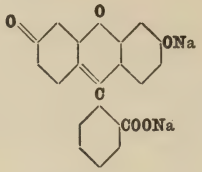
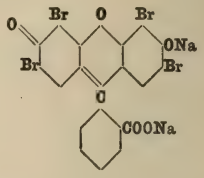
Colouring matter, .	*Soluble blue.**	*Methyl alkali blue.**
		
Description, . .	Violet crystals with coppery lustre.	Blue powder.
Solubility in Water, . .	Readily soluble.	Readily soluble.
Solubility in Alcohol, . .	Readily soluble.	Somewhat readily soluble.
Solubility in Ether, . .	Insoluble.	Soluble in traces.
Solubility in Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	Emits white vapour of an aromatic odour; chars and burns away, leaving white ash.	Melts, puffs up, chars, and then burns away, leaving only a little white ash.
Conc. H_2SO_4, .	Dissolves, forming dark brown-red solution; on dilution, blue; on heating, conc. solution becomes blackish-brown.	Dissolves, forming red-brown solution; on dilution, blue precipitate; filtrate colourless; on heating, conc. solution violet-black.
Dil. H_2SO_4, . .	Unchanged.	On heating, quantitative blue precipitate, not extracted by ether.
Sodium hydrate, .	Dark red solution.	On heating, becomes dark purple; on continued boiling, pale red.
Ammonia, . .	Dark red solution.	Same as with sodium hydrate.
Tannin reagent, .	Unchanged.	On heating, partial precipitation.
Alum, . . .	Unchanged.	Partial precipitation; on heating, separates more completely.
Potassium bichromate,	Unchanged.	Unchanged.
Stannous chloride, .	In the cold, mostly precipitated; on heating, partly soluble.	On heating, quantitatively precipitated, blue.
Zinc dust and ammonia,	Reduced; filtrate colourless; on addition of acetic acid, violet colour.	Somewhat quickly decolorised; filtrate pale blue.
Zinc dust and acetic acid,	Reduced with great difficulty, requires boiling; filtrate pale green.	Reduced with difficulty; in the filtrate the blue colour returns.

* The corresponding homo-derivative will always be present (see p. 86).

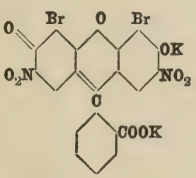
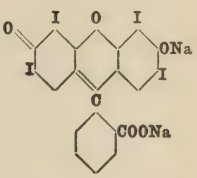
Pyronine Dyestuffs.

Colouring matter, .	*Fast acid violet* B. 	*Fast acid blue* R. 
Description, .	Red-violet powder.	Dark blue powder.
Solubility in: Water, . .	Dark rose-red solution.	Blue-violet solution.
Solubility in: Alcohol, . .	Pink solution.	Blue-violet solution.
Solubility in: Ether, . .	Insoluble.	Insoluble.
Solubility in: Benzene, . .	Soluble in traces.	Insoluble.
Heating on platinum foil,	Emits a violet, then a brown vapour; melts and burns away, leaving a fusible white ash.	Chars and leaves a quantity of grey ash.
Conc. H_2SO_4, . .	Orange-red solution; on dilution, red-violet; on standing, partial precipitation, bluish-red.	Brown-red solution; on dilution, completely precipitated, dark blue.
Dil. H_2SO_4, . .	Partial precipitation, violet-red; on heating, more soluble.	In the cold, completely precipitated, dark blue; on heating, slightly soluble, violet.
Sodium hydrate, .	Somewhat redder.	Solution in the cold, violet; on heating, red-violet.
Ammonia, . .	Somewhat redder.	Solution violet.
Tannin reagent, .	Unchanged.	Unchanged.
Alum, . . .	Partial precipitation, bluish-red.	Partial precipitation; on heating, dark blue; filtrate violet-red.
Potassium bichromate,	Clear solution; on heating, somewhat paler.	Dirty olive-green solution.
Stannous chloride, .	In the cold, almost completely precipitated, bluish-red; on heating, somewhat soluble.	Almost completely precipitated, dark blue; filtrate in the cold bluish; on heating, pale violet.
Zinc dust and ammonia,	Decolorised on standing.	Easily reduced; filtrate faint yellowish-red; on addition of acetic acid, pale violet.
Zinc dust and acetic acid,	Reduced on boiling; filtrate at once becomes pink.	Not reduced.

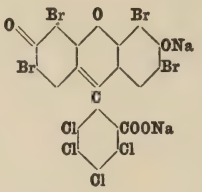
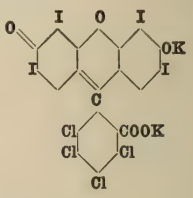
Pyronine Dyestuffs—*continued.*

Colouring matter, .	*Uranine.* 	*Eosine* A. 
Description, . .	Brown crystals with green metallic lustre.	Crystals with reddish metallic lustre.
Solubility in: Water, . .	Readily soluble; yellow with strong yellow-green fluorescence.	Very readily soluble; red with yellow fluorescence.
Solubility in: Alcohol, .	Readily soluble; orange with yellow-green fluorescence.	Soluble; very strongly fluorescent.
Solubility in: Ether, . .	Insoluble.	Insoluble.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	Swells up very strongly, melts, and then burns away, leaving fusible ash.	Burns away slowly and gradually, and leaves a white fusible ash.
Conc. H_2SO_4, . .	Dissolves, giving a yellow solution with green fluorescence; on dilution, yellow; the conc. solution, on heating, becomes dark brown-red.	Dissolves, giving a yellow solution; on dilution, quantitatively precipitated, orange-red; the conc. solution, on heating, becomes dark red.
Dil. H_2SO_4, . .	Fluorescence disappears almost entirely.	In the cold, and on heating, quantitative orange-red precipitate, extracted by ether.
Sodium hydrate, .	Unchanged.	Unchanged.
Ammonia, . .	Unchanged.	Unchanged.
Tannin reagent, .	Fluorescence disappears.	Fluorescence disappears.
Alum, . . .	In the cold, partial precipitation, orange-yellow; on heating, yellow solution.	Partial precipitation, orange-red.
Potassium bichromate,	Fluorescence disappears.	Unchanged.
Stannous chloride, .	In the cold, and also on heating, partial precipitation, orange-yellow.	In the cold, quantitative bright red precipitate; on heating, becomes deeper carmine-red.
Zinc dust and ammonia,	Quickly reduced; in the filtrate the colour returns.	Quickly reduced; filtrate bright pink with strong green fluorescence.
Zinc dust and acetic acid,	Quickly reduced; filtrate colourless.	Somewhat quickly reduced; filtrate reddish with slight fluorescence.

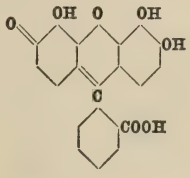
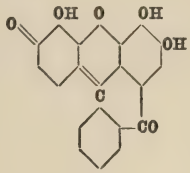
Pyronine Dyestuffs—*continued.*

Colouring matter, .	*Eosine scarlet* BB extra. *Eosine* BN.  	*Erythrosine.* 
Description, . .	Brown powder.	Brick-red powder.
Solubility in Water, . .	Readily soluble; red with slight green fluorescence.	Readily soluble; very slight yellow-brown fluorescence.
Solubility in Alcohol, . .	Readily soluble; carmine-red with yellow fluorescence.	Readily soluble with slight green-yellow fluorescence.
Solubility in Ether, . .	Soluble in traces.	Soluble in traces.
Solubility in Benzene, . .	Soluble in traces.	Soluble in traces.
Heating on platinum foil,	Explodes slightly, then chars and burns away with difficulty, leaving white fusible ash.	Emits iodine vapour, then chars, and finally leaves a fusible white residue.
Conc. H_2SO_4, . .	Dissolves with yellow colour; diluted, quantitative orange precipitate; on heating, conc. solution becomes dark brown-red.	Dissolves, giving dark yellow solution; on dilution, quantitative orange-red precipitate; the conc. solution, on heating, becomes dark red-brown and much iodine is given off.
Dil. H_2SO_4, . .	Quantitative orange precipitate, extracted by ether.	Quantitative scarlet precipitate, extracted by ether.
Sodium hydrate, .	Unchanged.	Unchanged.
Ammonia, . .	Unchanged.	Unchanged.
Tannin reagent, .	Fluorescence disappears.	Unchanged.
Alum, . . .	In the cold, partially precipitated; on heating, pale orange.	In the cold, quantitative bright red precipitate; on heating, scarlet; filtrate yellow.
Potassium bichromate,	Fluorescence disappears.	Unchanged.
Stannous chloride, .	In the cold, pale orange-red quantitative precipitate; on heating, pale red, somewhat soluble.	Quantitative red precipitate.
Zinc dust and ammonia,	Quickly reduced; filtrate and edges of the filter-paper carmine-red.	Quickly reduced; filtrate pale pink with strong green fluorescence; edges of the filter-paper yellow.
Zinc dust and acetic acid,	Reduced with great difficulty, even on boiling; filtrate orange-yellow (acetic acid precipitates the insoluble acid).	Reduced with great difficulty; filtrate yellowish with yellow-green fluorescence.

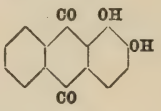
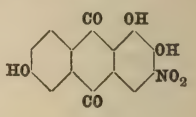
Pyronine Dyestuffs—*continued.*

Colouring matter, .	*Phloxine*. 	*Rose Bengal* 3B. 
Description, . .	Yellow-brown powder.	Brown-red powder.
Solubility in Water, . .	Readily soluble; strong yellow fluorescence.	Readily soluble; red without strong fluorescence.
Solubility in Alcohol, . .	Readily soluble; carmine-red with strong yellow fluorescence.	Readily soluble; carmine-red with golden-brown fluorescence.
Solubility in Ether, . .	Soluble in traces.	Insoluble.
Solubility in Benzene, . .	Soluble in traces.	Soluble in traces.
Heating on platinum foil,	Emits a brown vapour, chars, and then burns away, leaving white fusible ash.	Emits iodine vapour, then chars and finally burns away, leaving fusible white ash.
Conc. H_2SO_4, . .	Dissolves, giving dark orange-yellow solution; on dilution, quantitative pale red precipitate; the conc. solution, on heating, becomes red-brown.	Dissolves with golden-brown colour; diluted, quantitative flesh-coloured precipitate; on heating, conc. solution iodine is given off.
Dil. H_2SO_4, . .	Quantitative bright red precipitate, extracted by ether.	In the cold, and on heating, quantitative flesh-coloured precipitate, extracted by ether.
Sodium hydrate, .	Unchanged.	Unchanged.
Ammonia, . .	Unchanged.	Unchanged.
Tannin reagent, .	Unchanged.	Unchanged.
Alum, . . .	In the cold, bright red precipitate, almost quantitative; on heating, bright flesh colour, quantitative.	Almost quantitative bright red precipitate; on heating, becomes bright flesh colour.
Potassium bichromate,	Unchanged.	Unchanged.
Stannous chloride, .	Quantitative bright red precipitate.	Quantitative rose-red precipitate.
Zinc dust and ammonia,	Quickly reduced; filtrate pink with strong yellow fluorescence; edges of the filter-paper pink.	Quickly reduced; filtrate pale pink with strong yellow-green fluorescence.
Zinc dust and acetic acid,	Reduced with great difficulty; filtrate almost colourless (acetic acid precipitates the insoluble free acid).	Reduced with difficulty; filtrate colourless (acetic acid precipitates the insoluble free acid).

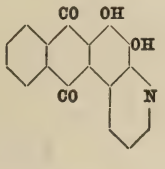
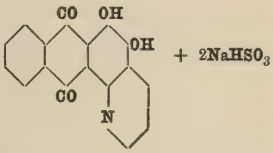
Pyronine Dyestuffs—*continued.*

Colouring matter, .	*Galleïne.* 	*Cœruleïne.* 
Description, . .	Brown paste.	Greenish-black paste.
Solubility in: Water, . .	In the cold, somewhat soluble, bluish-red; on heating, soluble, brown-red.	In the cold, insoluble; on heating, slightly soluble, pale green.
Solubility in: Alcohol, . .	Soluble; red-brown.	Somewhat soluble; blue-black.
Solubility in: Ether, . .	Soluble in traces.	Insoluble.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	After the evaporation of the water, the residue melts, brown vapour is emitted, the mass ignites and burns away, leaving no ash.	After evaporating the water, the black residue burns away, leaving no ash.
Conc. H_2SO_4, . .	Dissolves, forming a deep yellow-brown solution; on dilution, orange; on heating, conc. solution becomes dark brown.	Dissolves with a dark brown colour; on dilution, almost quantitatively precipitated, blackish-green.
Dil. H_2SO_4, . .	On heating, a deep orange solution.	Slightly soluble on heating.
Sodium hydrate, .	Violet-blue solution.	Olive-green precipitate; filtrate pale green.
Ammonia, . .	Dirty violet solution.	Olive-green solution.
Tannin reagent, .	...	...
Alum, . . .	On heating, a dark violet-red solution.	On heating, a green precipitate; filtrate pale green.
Potassium bichromate,	On heating, partially precipitated.	On heating, almost quantitatively precipitated.
Stannous chloride, .	Quantitatively precipitated; pale violet-red.	Quantitatively precipitated, greenish-grey.
Zinc dust and ammonia,	Rapidly decolorised; filtrate pale yellow.	Rapidly reduced; forms a red solution, quickly oxidising to green in the air.
Zinc dust and acetic acid,	...	...

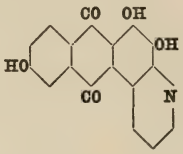
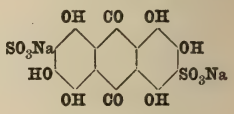
Anthracene Dyestuffs.

Colouring matter, .	*Alizarine.* 	*Alizarine orange* G. 
Description, . .	Brownish-yellow paste.	Yellow paste.
Solubility in Water, . .	Almost insoluble (even on boiling).	Slightly soluble; brownish-red.
Solubility in Alcohol, . .	Readily soluble; deep yellow.	Red-brown solution.
Solubility in Ether, . .	Fairly soluble; yellow.	Fairly soluble; yellow-green.
Solubility in Benzene, . .	Fairly soluble.	Fairly soluble; yellow-green.
Heating on platinum foil,	After evaporating the water, the Alizarine at first sublimes, then chars and burns away, leaving no ash.	Brownish-yellow dried powder, melts to a black liquid, sublimes, ignites, and finally burns away, leaving no ash.
Conc. H_2SO_4, . .	Dark yellowish-red solution; on dilution, yellow precipitate.	Brown-red solution; on dilution, almost completely precipitated.
Dil. H_2SO_4, . .	Unchanged.	Unchanged.
Sodium hydrate, .	Violet solution.	Dark brown-red solution.
Ammonia, . .	Red-violet solution.	Dark brown-red solution.
Tannin reagent, .	...	...
Alum, . . .	On heating, partly dissolves to form orange solution.	In the cold, unchanged; on heating, an orange-red precipitate.
Potassium bichromate,	On boiling, an orange-brown precipitate.	Unchanged.
Stannous chloride, .	Unchanged.	In the cold, unchanged; on boiling, brown precipitate.
Zinc dust and ammonia,	With zinc powder, orange-red; on filtering and warming the filtrate original colour restored.	Reduced on boiling; yellowish-green; filtrate rapidly becomes dark brown.
Zinc dust and acetic acid,	...	...

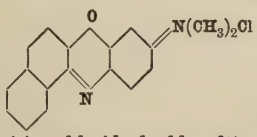
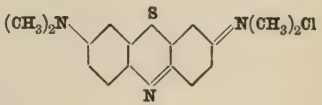
Anthracene Dyestuffs—*continued.*

Colouring matter, .	*Alizarine blue.* 	*Alizarine green* S. 
Description, . .	Greyish-blue paste.	Reddish brown paste.
Solubility in Water, . .	Insoluble.	Red-violet solution.
Solubility in Alcohol, . .	Soluble ; greyish-blue solution.	Violet-red solution.
Solubility in Ether, . .	Fairly soluble ; reddish.	Soluble in traces.
Solubility in Benzene, . .	Fairly soluble ; red.	Soluble in traces.
Heating on platinum foil,	After the evaporation of the water, a reddish vapour is emitted, the mass then chars and burns away, leaving no ash.	Carbonises quickly, leaving a greyish-white ash.
Conc. H_2SO_4, . .	Dissolves, forming violet-red solution ; on dilution, pale red ; on heating, conc. solution becomes dark brown.	Ruby-red solution ; brown precipitate on dilution ; on heating, becomes darker.
Dil. H_2SO_4, . .	In the cold, dirty brown precipitate ; filtrate pale red.	In the cold, unchanged ; on heating, a greenish-grey precipitate.
Sodium hydrate, .	Forms blue solution ; with excess of alkali, green.	Ruby-red solution.
Ammonia, . .	Forms greenish-blue solution.	Ruby-red solution.
Tannin reagent, .	...	Slight grey precipitate.
Alum, . . .	Blue-black precipitate on heating.	Violet solution.
Potassium bichromate,	Blackish precipitate.	Red-brown solution.
Stannous chloride, .	Blackish precipitate.	In the cold, dirty violet turbidity ; on heating, completely precipitated, greyish-green.
Zinc dust and ammonia,	Reduces to red solution ; filtrate reoxidised to blue on exposure to the air.	Reduced on boiling, brownish filtrate at once becomes dark red-brown.
Zinc dust and acetic acid,	...	...

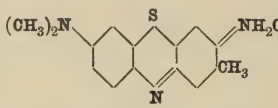
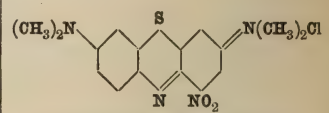
Anthracene Dyestuffs—*continued.*

Colouring matter, .	*Alizarine black* P. 	*Acid alizarine blue* BB. 
Description, . .	Greyish-black paste.	Red-brown powder.
Solubility in: Water, . .	Somewhat soluble; olive.	Soluble with a carmine-red colour.
Solubility in: Alcohol, . .	Somewhat soluble; brownish.	Slightly soluble; red.
Solubility in: Ether, . .	Slightly soluble; brownish-yellow.	Soluble in traces.
Solubility in: Benzene, . .	Soluble in traces.	Insoluble.
Heating on platinum foil,	Dries, forming a black mass, which melts, gives a brown sublimate, and then burns away, leaving no ash.	Melts and burns away, leaving white ash.
Conc. H_2SO_4, . .	Dark brown solution; on dilution, yellow-brown precipitate; filtrate orange.	Dissolves, forming red-violet solution; on dilution, red.
Dil. H_2SO_4, . .	Brown residue; filtrate, when cold, pale yellow.	Red solution; unchanged on boiling.
Sodium hydrate, .	Greyish-green solution.	Blue solution; on standing, blue precipitate.
Ammonia, . .	In the cold, brownish-black solution; on boiling, reddish-black.	Blue solution; not precipitated on standing.
Tannin reagent, .	...	On heating, a brick-red precipitate; filtrate orange.
Alum, . . .	Black precipitate.	Red-violet solution.
Potassium bichromate,	Black precipitate.	On heating, dark brown solution.
Stannous chloride, .	Reddish-grey precipitate.	Completely precipitated, red-violet.
Zinc dust and ammonia,	Reduced on boiling; filtrate brown-red, rapidly becoming darker.	At first a blue coloration; then decolorised, giving a colourless filtrate.
Zinc dust and acetic acid,	...	Reduced, forming a brick-red solution.

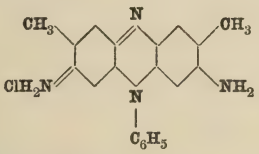
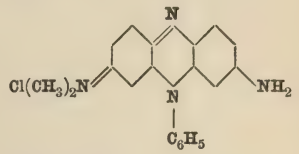
Oxazines and Thiazines.

Colouring matter, .	*Meldola's blue.*  (zinc chloride double salt).	*Methylene blue.* 
Description, . .	Violet, crystalline.	Small crystals with greenish metallic lustre.
Solubility in: Water, . .	Readily soluble.	Readily soluble.
Solubility in: Alcohol, . .	Sparingly soluble.	Readily soluble.
Solubility in: Ether, . .	Insoluble.	Insoluble.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	Emits white vapour, burns with crepitation, chars, and finally burns away, leaving a quantity of infusible ash (zinc oxide).	Emits a greenish vapour, burns with a smoky flame, chars, and then burns away, leaving no ash.
Conc. H_2SO_4, .	Dissolves, with evolution of **HCl**; solution brown; on dilution, blue.	Dissolves with evolution of **HCl**; solution grass-green; diluted with water, blue.
Dil. H_2SO_4, . .	Unchanged.	Unchanged.
Sodium hydrate, .	On heating, completely decolorised; brown precipitate.	Violet-blue solution; excess of strong caustic soda produces precipitate; extracted by ether.
Ammonia, . .	On heating, completely decolorised; brown precipitate.	Unchanged.
Tannin reagent, .	Blue precipitate.	Quantitative blue precipitate, somewhat soluble on boiling.
Alum, . . .	Unchanged.	Unchanged.
Potassium bichromate,	Unchanged.	Quantitative red-brown precipitate; on heating, olive-green, partly soluble.
Stannous chloride, .	On heating, quantitative blue precipitate.	Quantitative dirty blue precipitate, becoming colourless on heating.
Zinc dust and ammonia,	Easily reduced; filtrate colourless; on addition of acetic acid, colour restored.	Quickly reduced; the filtrate and edges of the filter-paper rapidly become violet.
Zinc dust and acetic acid,	Quickly reduced; filtrate colourless, slowly becoming blue.	Easily reduced; filtrate and edges of the filter-paper rapidly become blue.

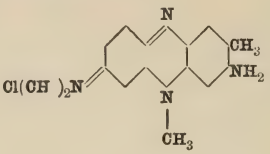
Oxazines and Thiazines—*continued.*

Colouring matter, .	*Toluidine blue* O.  (zinc chloride double salt).	*Methylene green.*  (zinc chloride double salt).
Description, . .	Dark olive-green powder.	Dark brown powder.
Solubility in: Water, . .	Blue solution.	Readily soluble; blue-green.
Solubility in: Alcohol, . .	Blue-violet solution.	Readily soluble.
Solubility in: Ether, . .	Soluble in traces.	Insoluble.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	Melts, swells up, emits much strongly smelling vapour, and finally burns away, leaving a residue of zinc oxide.	Emits a little greenish vapour and swells up, then burns away, leaving residue of **ZnO**.
Conc. H_2SO_4, . .	Green solution, **HCl** evolved; on dilution, blue-green; conc. solution, on heating, violet-black; diluted, red-violet.	Dissolves with evolution of **HCl**; solution bluish-green; diluted, greenish-blue; on heating, conc. solution becomes black-violet.
Dil. H_2SO_4, . .	Unchanged.	Unchanged.
Sodium hydrate, .	In the cold, almost quantitative brown-violet precipitate; mostly soluble on boiling.	Almost quantitative violet precipitate, extracted by ether.
Ammonia, . .	Slight dark violet precipitate; filtrate violet.	Partial precipitation, blue-black; extracted with ether.
Tannin reagent, .	In the cold, almost quantitative dark blue precipitate, slightly soluble on heating.	Quantitative blue-green precipitate, dissolves on heating.
Alum, . . .	Unchanged.	Unchanged.
Potassium bichromate,	In the cold, complete precipitation, dark brown; on heating, almost clear green solution.	Completely precipitated, brown-black.
Stannous chloride, .	In the cold, almost complete precipitation, pale blue; on boiling, decolorised.	Quantitative dirty green precipitate, which, on filtering, quickly becomes paler.
Zinc dust and ammonia,	Easily reduced, colourless; filtrate at once becomes red-violet.	Quickly reduced; the filtrate and edges of the filter-paper rapidly become violet.
Zinc dust and acetic acid,	Easily reduced, colourless; filtrate at once becomes pale blue.	Reduced with some difficulty, filtrate and edges of the filter-paper rapidly become blue.

Safranines and Indulines.

Colouring matter, .	*Safranine.* 	*Methylene violet.* 
Description, . .	Brown powder.	Brown powder.
Solubility in: Water, . .	Readily soluble; red solution.	Soluble with wine-red colour.
Solubility in: Alcohol, . .	Readily soluble; red with yellow fluorescence.	Soluble with wine-red colour.
Solubility in: Ether, .	Insoluble.	Soluble in traces.
Solubility in: Benzene, . .	Insoluble.	Insoluble.
Heating on platinum foil,	A red vapour is given off; the mass melts, ignites, chars, and finally burns away, leaving no ash.	Puffs up strongly, emitting a violet vapour, chars, and finally burns, leaving no residue.
Conc. H_2SO_4, .	Dissolves with evolution of **HCl**, solution green; diluted, becomes blue, violet, and finally red; the conc. solution, on heating, becomes blackish-olive.	Dissolves with evolution of **HCl**, green solution; on dilution, becomes blue, then violet, and finally wine-red.
Dil. H_2SO_4, . .	Partial dirty orange-red precipitate; dissolves on heating.	Somewhat darker and bluer on heating.
Sodium hydrate, .	Partial red-brown precipitate, extracted by ether.	In the cold, little change; on heating, colour base slowly separates.
Ammonia, . .	No precipitate.	Unchanged.
Tannin reagent, .	Partial precipitation of the lake.	Partial red-violet precipitate.
Alum, . . .	Unchanged.	Unchanged.
Potassium bichromate,	Quantitative red precipitate, more soluble on heating.	Brown precipitate, which redissolves on boiling.
Stannous chloride, .	Partial buff-coloured precipitate; dissolves on heating.	Fine red-violet precipitate.
Zinc dust and ammonia,	Easily reduced; the colour is restored immediately.	Colour incompletely destroyed.
Zinc dust and acetic acid,	Easily reduced; the colour is restored immediately.	Reduced to a bright yellow solution; partially restored on exposure to the air.

Safranines and Indulines—*continued.*

Colouring matter, .	*Azine scarlet* G. 	*Induline* (spirit soluble). See page 163.
Description, . .	Brown powder.	Brown-black powder.
Solubility in: Water, . .	Readily soluble, boiling; red solution.	Sparingly soluble; violet.
Solubility in: Alcohol, .	Readily soluble; the solution exhibits a strong fluorescence.	Dark violet solution.
Solubility in: Ether, . .	Insoluble.	Red solution.
Solubility in: Benzene, . .	Insoluble.	Red solution.
Heating on platinum foil,	Carbonises and leaves little ash.	Melts, swells up, emits violet vapours, chars, and finally burns away, leaving no ash.
Conc. H_2SO_4, . .	HCl evolved; blue-green solution; on dilution, partial red-brown precipitate.	Blue-violet solution; diluted, violet; on standing, partial violet precipitate.
Dil. H_2SO_4, . .	In the cold, red turbidity; on boiling, original colour restored.	Unchanged.
Sodium hydrate, .	Unchanged.	In the cold, completely precipitated, red; on boiling, somewhat soluble.
Ammonia, . .	Unchanged.	The same as with sodium hydrate.
Tannin reagent, .	Scarlet-red precipitate, dissolves on boiling.	Completely precipitated, violet.
Alum, . . .	Unchanged.	In the cold, partial precipitation, violet; on heating, clear violet solution.
Potassium bichromate,	Brown precipitate, insoluble on boiling.	In the cold, completely precipitated, brown-violet; the precipitate almost entirely soluble on boiling.
Stannous chloride, .	Complete precipitation, dirty red.	In the cold, almost completely precipitated, violet; on heating, partly soluble.
Zinc dust and ammonia,	Solution rapidly decolorised; filtrate colourless; colour more or less restored on exposure to air.	Decolorised; filtrate at once becomes pink; with acetic acid, violet-red.
Zinc dust and acetic acid,	Solution quickly reduced; on exposure to air the colour is more or less restored.	Reduced, yellow; filtrate remains yellow-brown.

The examination of unknown dyestuffs.—For the purpose of detecting the composition of an unknown dyestuff or a mixture of dyestuffs, the method of Rota (*Chem. Zeit.*, 1898, 437), which depends on the behaviour of dyestuffs when treated with a solution of $SnCl_2 + HCl$, is of value. When the dyestuff is treated with a dilute solution of this reagent (1 : 10,000) until the boiling-point is reached, only members of certain classes are reduced, these being derivatives of mono- and diimido-quinones, while those derived from a quinone containing one diatomic carbon group instead of an oxygen atom in the quinone ring are not reduced.

Thus the reducible colours are derivatives, such as nitro-, nitroso-, azo-, and quinoneimide colours of

O=R=N–	or	–N=R=N–
oximidoquinone		diimidoquinone.

Those not reducible are the following, such as the oxyquinone and triphenylmethane dyestuffs :—

O=R=C=	and	–N=R=C=
oxycarboquinone		imidocarboquinone.

If the solutions reduced by $SnCl_2$ are examined, it is found that some of them, after adding a few drops of ferric chloride, or even by shaking the solution, previously neutralised with KOH, in air, remain unchanged ; while others are oxidised to the original colour.

The former are the nitro-, nitroso-, and azo-colours, which yield stable amines on reduction ; the latter are the quinoneimide derivatives, yielding leuco-bases which are easily reoxidised.

The unreducible colours can be divided into two groups according to whether they are derived from oxycarboquinone or imidocarboquinone. To the latter belong the Magentas, Acridines, etc., which, when warmed in aqueous solution with KOH, are decolorised or precipitated ; the former, by reason of their acid character, yield, with alkalies, bright-coloured salts which are usually soluble.

The dyestuffs can be thus divided into four classes, to which two or three large groups with similar chromophores belong.

The further division of these dyestuffs into single families is founded on the different nature of the salt-yielding groups in them. The question whether the dyestuffs contain amido- or imido-groups, carboxyl or sulphonic groups, has then to be dealt with. For this purpose the use of ether and the different fibres (cotton, wool, etc.) is of great service.

A. Classification of the Organic Dyestuffs.

A portion of the aqueous or dilute alcoholic solution of the dyestuff is treated with **HCl** and then with **$SnCl_2$**.*

It is completely decolorised :—		The colour does not alter, and remains the same as with **HCl** alone.	
Reducible Dyestuffs.†		*Non-reducible Dyestuffs.*	
The decolorised solution is treated with **$FeCl_3$** solution, or with air, after neutralisation with **KOH** (or sodium acetate).		A portion of the original solution is treated with a 20 per cent. solution of **KOH** and warmed.	
The solution remains colourless.	The original colour is restored.	The solution is decolorised, or a precipitate is formed.	No precipitate is formed, and the liquid becomes intensely coloured.
Dyestuffs not reoxidised after reduction.	Dyestuffs reoxidised after reduction.	Quinoneimido - dyestuffs.	Quinone dyestuffs.
Class I.	Class II.	Class III.	Class IV.

* The aqueous or alcoholic solution should contain 1 part of dyestuff in 10,000 parts solvent, and 5 c.c. of this mixed with 4–5 drops of concentrated hydrochloric acid and then with a similar quantity of **$SnCl_2$** (10 per cent. solution prepared by dissolving tin in hydrochloric acid). The mixture should be shaken and, if necessary, heated to boiling. If decolorisation is only partial, more tin solution may be added, or the dye solution may be further diluted.

† Certain indulines are only decolorised with difficulty, and do not give completely colourless solutions.

After having separated the colours according to the foregoing table, their identification is much simplified by the help of the detailed properties and reactions of typical dyestuffs already given.[1] For the detection of bromine or iodine the solution of the dyestuff is boiled with zinc dust and **KOH**, and the filtered solution, after being acidified with acetic acid, tested with chlorine water or starch solution. The dyestuff may also be ignited with **CaO**, the residue treated with nitric acid, and the halogen in the solution tested for in the usual way. To determine the presence of sulphur, in order, for instance, to distinguish between the thiazines and the oxazines, the substance is melted with nitre and the melt tested for sulphuric acid.

In case the colour can be reduced, the tin is removed by treatment with **H_2S** and the product examined. Thus the azo-compounds yield a mixture of at least two primary amines, according to the equation

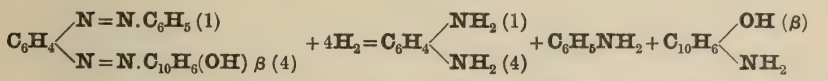
$$R-N=N-R_1+2H_2=R-NH_2+R_1-NH_2$$

These can sometimes be easily separated by ether; the reduced solution is treated with **H_2S** to remove tin, and the solution rendered alkaline with **KOH**, extracted with ether, which dissolves the non-sulphonated amine, while the sulphonated amine remains in the aqueous solution. The latter can often be combined with certain diazo-salts, giving a definite dyestuff which may easily be recognised.

[1] More information on this subject can be obtained from such books as Green, *Organic Colouring Matters*, and Lehne, *Tabellar. Uebersicht der künstl. organ. Farbstoffe.*

When a *para*diamine is obtained (by the reduction of an amidoazo-compound), this is recognised by the *thiazine* reaction, *i.e.* treating the solution (free from tin) with HCl and $FeCl_3$ in presence of H_2S.

A *para*diamine is also obtained by the reduction of a *dis*azo-dyestuff; thus, for instance, Sudan III [A] on reduction gives



In the case of a dyestuff containing no amido-group, this reaction is helpful in distinguishing between a *mono*azo- and a *dis*azo-dyestuff.

It is also possible to decide whether, when an SO_3H group is present, this is in the middle or one of the end radicles, for the thiazine formed from a non-sulphonated diamine is soluble in ether (in presence of KOH), while that from a diamine containing a sulphonic acid group remains in the aqueous solution.

The examination of mixtures of dyestuffs.—The difficulty of detecting and identifying dyestuffs is much increased in the case of mixtures. A preliminary examination may be made by examining the powder under a microscope, or blowing a little of the powder upon sulphuric acid or moistened filter-paper, etc. Separation by means of water or alcohol may be tried, although mixtures of dyestuffs usually resist this method of separation, owing to the similarity of the components.

Much use, however, may be made of ether and wool in this examination. The free base of a basic colour is easily extracted from its alkaline solution by ether or wool. In the case of an acid dyestuff, the colour acid is liberated by means of a stronger acid, and then the colour (in the form of the free acid) is extracted with ether or wool.

Both agents should be used, as some dyestuffs which are extracted with ether do not dye wool.

Separation by means of ether.—The object of this is chiefly to distinguish between basic and acid dyestuffs. The former are extracted with ether from their dilute alkaline solutions, while the latter remain in the aqueous solution. The operation is carried out as follows:—100 c.c. of the aqueous solution of the dyestuff is treated with 1 c.c. of a 20 per cent. KOH solution and shaken with three times its volume of ether; this shaking is repeated with fresh ether until the latter is no longer coloured even after acidifying it (the ether) with acetic acid. The aqueous alkaline solution of the acid dyestuff is neutralised with acetic acid and put aside for later examination. The ethereal solution of the colour-base is washed with an equal volume of very slightly alkaline water, and finally shaken with one-third its volume of 5 per cent. acetic acid. This acid solution is withdrawn from the ethereal layer and evaporated on the water-bath; the residue contains the basic dyestuff. Occasionally the dyestuff remains undissolved by the acetic acid, in which case the ethereal solution remains coloured and must be evaporated on the water-bath in order to obtain the colour-base. A very few neutral dyestuffs are also extracted by ether, *e.g.* Quinoline yellow, Indophenol blue (spirit soluble), the different Sudans, etc. All these are insoluble in water and soluble in alcohol; they are extracted by ether even from their acid solutions and also remain dissolved after treatment with water or dilute acid.

In the extraction of basic colours with ether it is not entirely immaterial which alkali is used; all bases are set free by potash. Other alkalies, such as, *e.g.*, ammonia, are not in many cases sufficiently strong. Other bases, again, are readily extracted by ether in the absence of any alkali. Thus, for instance, Safranine, which is a very strong base, requires the use of potash, while Magenta is liberated by ordinary ammonia; others, such as the Indulines, Oxazines, and

Acridine, are set free by very dilute ammonia; and finally such colours as Chrysoïdine, Bismarck brown, Rhodamine S [By], Victoria blue, etc., are dissociated in their aqueous solution, and the base passes into the ether, while the acid remains in the water. This difference is made use of in analysis. The dilute aqueous solution is first extracted with ether, and the extraction continued (with fresh ether) after adding successively 1 per cent. ammonia, concentrated ammonia, and, lastly, 20 per cent. potash. A further separation depends on the different solubilities of bases in water and ether. When the ethereal solution is shaken with an equal volume of water, some bases pass into the latter, while others remain dissolved in the ether. In this way it is possible to separate Acridine yellow from the very similar dyestuff Phosphine.

The bases remaining dissolved in the ether can be separated by extracting with 5 per cent. acetic acid; some are dissolved and can be recovered from the acid solution, while others remain behind.

The acid dyestuffs which were not extracted from the alkaline solution by ether are separated by similar methods. The neutral solution is acidified with hydrochloric or sulphuric acid and extracted with ether; the non-sulphonated acids are dissolved, while most of the sulphonated ones remain behind. Some, however, of the latter are partly soluble in ether, *e.g.* Roccelline, Ponceau G [B], Wool black, Azoflavine, etc. This latter difficulty is overcome by the use of 1 per cent. acetic acid, instead of the mineral acid, when the sulphonated acids remain entirely undissolved by the ether.

The acid dyestuffs can thus be divided into three classes, viz. :—(1) Soluble in ether in presence of 1 per cent. acetic acid; (2) soluble in ether in presence of hydrochloric or sulphuric acid; (3) insoluble in ether.

By this means we can separate Erythrosine [B] from Roccelline and Bordeaux B [A], also Direct yellow [A] from Congo brown R [A] and from Congo red [A].

If the mixture consists entirely of acid dyestuffs, we obtain a fourth class, viz. :—those dyestuffs which are extracted by ether from the neutral solution, *e.g.* Sudan I. [A] and Sudan G [A]. In this way Sudan G [A] can be separated from Victoria yellow, etc. The ethereal solution can in this case be washed with water in order to obtain a further separation, as already indicated; thus, *e.g.*, Picric acid is distinguished from Martius' yellow (the free dinitronaphthol is only very slightly soluble in water), and Diamond black from Naphthol orange.

Separation of dyestuffs by wool.—If the separation by ether cannot be carried out, the separation by wool is adopted. This fibre fixes all basic colours in weakly alkaline or neutral bath, while the acid colours remain in solution. This is, of course, equally a separation of acid and basic dyestuffs.

The method of working is as follows:—To 100 c.c. of a solution of the dyestuff (1 : 1000) 4–5 drops of ammonia are added, and then a skein of wool put in and the solution heated to boiling for three to five minutes. More wool may be put in as long as the colour is extracted. The dyed wool is washed with boiling ammonia water, then with pure water, and lastly extracted hot with 5 per cent. acetic acid; this solution is evaporated on the water-bath, yielding the basic dyestuffs. When a mixture of the latter is present in the original powder, a separation may often be brought about by dyeing the wool fractionally, varying the strength of ammonia or acetic acid, etc.

The separation of the acid dyestuffs is carried out as follows:—A 0·1 per cent. solution of dyestuff is prepared, and to each 100 c.c. are added 3–4 drops of concentrated hydrochloric acid. The solution is boiled and the skein dipped in and stirred for three to five minutes; a second and a third skein may be added till the last is no longer coloured. The direct colours are in this way absorbed by the wool, the indirect being left in the bath. The dyed skeins are washed with weakly acid water, then with pure water, and finally extracted with a boiling 5 per

cent. ammonia solution. From the latter the ammonia is boiled off and the direct colours are left in the neutral solution.

As some indirect dyestuffs are slightly fixed by wool, the dyeing experiment must be repeated with the solution thus obtained.

In this way it is possible to separate

Direct, . .	Bordeaux B [A].	Biebrich scarlet.	Acid yellow [A].
Indirect, . .	Eriocyanine.	Cochineal.	Turmeric.

If the dyeing be carried out first in neutral solution and then in acid solution, we can distinguish between

Fixed in neutral bath, . .	Alkali violet [B].	Acid violet 4BN.
„ acid „ . .	Ponceau 6RB [A].	New coccine [A], etc.

If the dyeing is carried out in a strongly acid solution (1 c.c. **HCl** to 200 c.c. solution), the following separation is possible :—

Fixed in strongly acid bath, . .	Bordeaux S [A].	Bordeaux B [A].
„ weak „ . .	Orange G [A].	Methyl orange.

In each case the wool is washed with pure, weak, or strongly acidified water according to the nature of the bath, and afterwards extracted with hot dilute ammonia.

In case a separation cannot be effected by means of either ether or wool, cotton should be tried. Among the colours dyeing cotton direct are Pyronine, Rhodamine (partly), Thioflavine among the basic; and Curcumine, the tetrazo-dyestuffs, Clayton yellow, etc., among the acid dyestuffs. The separation is effected by boiling for ten minutes in a neutral or soap bath, the cotton being finally washed well with boiling water. In this way can be separated

Direct for cotton, . .	Carbazol yellow [B].	Cotton yellow R [B].
Indirect „ . .	Diamond yellow R [By].	Phloxine B [B].

A separation may often be brought about by altering the reaction and concentration of the dye-bath. Thus in a slightly acid bath (**HCl**) the following two dyestuffs can be separated :—

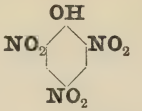
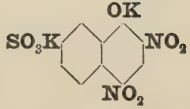
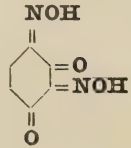
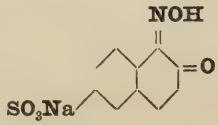
Easily fixed, . . .	Brilliant Congo [A].
Difficultly „ . . .	Brilliant yellow [A].

When all the above methods fail, different solvents may be tried, *e.g.* petroleum ether, amyl alcohol, chloroform, etc. The first of these can be used for separating Eosine from Martius' yellow.

The following are the special tables worked out by Rota for carrying out this method of analysis :—

[Table B.

B. Class I.—Dyestuffs reduced by $SnCl_2 + HCl$ and not again oxidised.

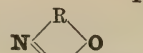
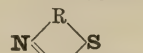
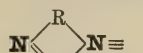
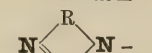
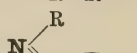
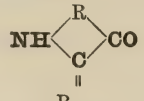
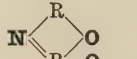
			Type.	
Nitro-dyestuffs R. NO_2 — Yellow or orange, soluble in water; direct for silk and wool, not for cotton; with $SnCl_2 + HCl$ partially reduced.	Nitrophenols (naphthols), insoluble in ether from KOH solution.	*Not sulphonated.* Soluble in ether in the presence of acetic acid.		Picric acid.
		Sulphonated. In all cases insoluble in ether.		Naphthol yellow S.
Nitroso-dyestuffs — Brown or green dyestuffs, mostly insoluble in water; all give with $H_2SO_4 + C_6H_5OH$ (Liebermann's reaction) blue colorations.		*Not sulphonated.* Insoluble in water, soluble in alcohol, soluble in ether in the presence of acetic acid.		Fast green O.
		Sulphonated. Soluble in water, insoluble in ether, ...		The iron lake is Naphthol green B.
Azo-dyestuffs R – N = N – R — The aqueous solution of these dyestuffs, on treatment with KOH and extraction with ether, give ethereal solutions, which, after washing with water, behave in the following way:—	Coloured: gives the original colour on shaking with dilute acetic acid.	*Not sulphonated.* Amidoazo-compounds (basic azo-dyestuffs).	$C_6H_5N : NC_6H_4(NH_2)_2HCl$	Chrysoïdine.
	Coloured solution: unaltered on shaking with dilute acetic acid.	*Not sulphonated.* Oxyazo-compounds.	$C_6H_5N : NC_{10}H_7(OH)\beta$	Sudan I.
	Colourless solution: unaltered by dilute acetic acid.	*Not sulphonated.* Extracted by ether from dilute acetic acid solution. — Oxyazo-dyestuffs with carboxyl groups. — For cotton indirect.		Diamond yellow.
			For cotton direct.	Chrysamine.
		Sulphonated. Not extracted by ether from dilute acetic acid solution. — Not acted upon by HNO_2.* — For cotton indirect.		Brilliant orange.
			For cotton direct.	Azo blue.
		Altered by HNO_2.* — For cotton indirect.		Fast yellow.
			For cotton direct.	Congo red.

* The action of nitrous acid is tested in the following way:—5 c.c. of the solution are treated with 2–3 drops of a 1 per cent. solution of acetic acid, and the same quantity of a 1 per cent. solution of $NaNO_2$, and warmed.

C. Class II.—Dyestuffs reduced by $SnCl_2 + HCl$ and re-formed on oxidation.

The aqueous or alcoholic solution is treated with **KOH** and extracted with ether.*

The ether solution washed with water behaves as follows :!

			Type.	
The ethereal solution is coloured or colourless; it gives, however, the original colour on treatment with 5 per cent. acetic acid (colour remains in acetic acid layer). *Basic dyestuffs*	The solution is easily reduced by $SnCl_2 + HCl$ in the cold.	Oxazines, . .		Meldola's blue.
		Thiazines, . .		Methylene blue.
	The coloured solution is reduced with difficulty, usually incompletely, and only after adding a large quantity of $SnCl_2 + HCl$ and heating.	Indulines,† . .		Induline (spirit soluble).
		Safranines, . .		Safranine.
Coloured; not changed by dilute acetic acid. *Neutral dyestuffs.* Insoluble in water, soluble in alcohol.	Blue; altered by **HCl** on warming.	Indophenol, . .		Indophenyl.
	Red or blue dyestuff, unaltered by **HCl**; gives with HNO_3 isatine.	Indogenide, . .		Indigotine.
Colourless; unchanged by acetic acid. *Acid dyestuffs.*	*Not sulphonated.* Soluble in ether in the presence of acetic acid.	Oxazone, . .		Fluorescent blue.
	Sulphonated. In all cases insoluble in ether.	Readily reduced by $SnCl_2 + HCl$	Sulphonated Indogenide.	Indigo-carmine.
			Sulphonated Thiazine.	Thiocarmine.
		Reduced with difficulty.	Sulphonated Indulines.	Induline soluble.

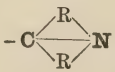
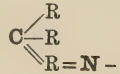
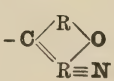
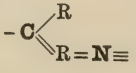
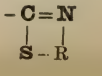
* The dilute dye solution (1 : 10,000), aqueous or alcoholic (5 c.c.), is treated with 4–5 drops of 20 per cent. **KOH**, and extracted with 10–15 c.c. ether. The ether solution is washed once with water, if the extracted solution is aqueous; if alcoholic, two or three times.

† The difference between the Indulines and the Safranines is as follows :—The colour-bases of the former are produced when its salts are treated with ammonia; the bases of the latter only by the action of **KOH**.

D. Class III.—Dyestuffs which are not reduced by $SnCl_2 + HCl$ and which contain the Chromophore.

$$=C=\langle\bigcirc\rangle=N-$$

The aqueous or alcoholic solution of the dyestuff is treated with **KOH** and extracted with ether.

			Type.	
The ether solution is colourless or coloured. The colour is extracted with 5 per cent. acetic acid. *Basic dyestuffs.*	The ether solution is colourless. The yellow aqueous (acetic acid) solution is decolorised by **KOH** and decomposed by **HCl**.	Auramines, . . .		Auramine (base).
	Ether solution greenish fluorescent. The aqueous solution of the dyestuff is precipitated by **KOH** and unchanged by **HCl**; HNO_3 produces red colour.	Acridines, . . .		Phosphine.
	Ether solution is coloured or colourless, not fluorescent. The colour extracted by acetic acid is red-violet, blue, and green without fluorescence. The aqueous solution is for the most part decolorised by **KOH**; and by **HCl** (with the exception of phenylated Magenta) is coloured yellow.	Magenta; not sulphonated.		Magenta.
	The ether solution is colourless; acetic acid extract red fluorescent colour. The aqueous solution is decolorised by **KOH**.	Pyronines (coloured yellow by **HCl**).		Pyronine G.
		Rhodamine (not sulphonated, unchanged by **HCl**)		Rhodamine S.
The coloured ether solution is not extracted by acetic acid. *Neutral dyestuffs.* Insoluble in water, soluble in alcohol.	The ether solution is yellow and not fluorescent. The alcoholic solution is yellow, not fluorescent, and is unchanged by acids or alkalies.	Quinophthalone, .		Quinoline yellow (spirit soluble).
The ether solution is colourless, and is not altered by acetic acid. *Acid dyestuffs.*	The aqueous solution of the dyestuff is boiled with pure cotton. The colour is not fixed on the cotton. Yellow dyestuff, soluble in water without fluorescence, unchanged by water, acids, or alkalies.	Sulphonated Quinophthalone.		Quinoline yellow (water soluble).
	Soluble dyestuff, red-violet, blue, or green; for the most part decolorised by **KOH**, little changed by **HCl**.	Sulphonated Magentas.		Acid magenta.
	Red or violet dyestuff, soluble in water with fluorescence; precipitated by **HCl**, unchanged by **KOH**.	Sulphonated Rhodamines.		Violamine R.
	The colour is fixed. Brown-yellow or orange dyestuff; aqueous solution more or less fluorescent.	Thiazols, . .		Primuline.

E. Class IV.—Dyestuffs which are not reduced by $SnCl_2 + HCl$ and which contain the Chromophore

$$=C=\langle\bigcirc\rangle=O$$

The alcoholic solution of the dyestuff is treated with a few drops of a dilute (1 : 1000) solution of $FeCl_3$.

- **Remains unchanged:—Triphenylmethane derivatives containing no amido-groups.** — The dyestuff is dissolved or suspended in boiling water.
  - Does not fix itself upon wool; is for the most part insoluble in water, soluble in water without fluorescence. — **Aurines**, . . . — Type: Aurine.
  - Is absorbed by wool; soluble in water and alcohol with fluorescence. — **Phthaleïns**, . . — Type: Eosine.
- **Is coloured green or olive green.** *Oxyketone dyestuffs.* — The original dyestuff is treated with weak alkali. (**KOH**, 1 per cent.).
  - Dissolves with a yellow or red-yellow colour. Monoketones. — The alkaline solution is treated with excess of **HCl**.
    - Tends to become decolorised (with decomposition). — **Benzophenones**, . — Type: Alizarine yellow A.
    - Is coloured intense yellow, without decomposition. — **Flavones**, . . — Type: Quercetine.
  - Dissolves with a red, red-violet, violet, blue, or green colour. Diketones. — The alkaline solution is acidified with acetic acid.
    - The free colour acid is precipitated; soluble in ether, and indirect for the fibre. — **Anthraquinones, not sulphonated.** — Type: Alizarine.
    - The free colour acid remains in solution; is insoluble in ether and colours wool direct. — **Anthraquinones, sulphonated.** — Type: Sulphonated alizarines.

Separation of Dyestuffs by Adsorption.

That certain dyestuffs are adsorbed by materials, such as starch, kaolin, talc, pumice stone, kieselguhr, etc., has been known for a considerable time, and the adsorbing properties of these materials have been studied especially by Suida (*Monatsh.*, 1904, xxv. 1107) and Dreaper (*7th Inter. Congr. Appl. Chem.*, London, 1909; *J.S.C.I.*, 1909, xxviii. 700).

Kaolin, in particular, is one of the best adsorbing agents, and its use for the separation of dyestuffs, especially when occurring in foodstuffs, has been investigated by Chapman and Siebold (*Analyst*, 1912, xxxvii. 339). Ten c.c. of the dye solution (containing about 1 gram of the dyestuff per litre) are stirred for several minutes with 5 grams of kaolin previously mixed with 10 c.c. of water, and the mixture is filtered through a Büchner funnel by the aid of the pump. The following table shows the behaviour of a number of dyestuffs when treated in this manner:—

Adsorbed.	Partially Adsorbed, but Adsorbed Colour partly extracted by Washing with Water.	Not Adsorbed.
Congo red.	Acid green.	Acid magenta.
Safranine.	Patent blue.	Eosine.
Magenta.	Soluble blue.	Erythrosine.
Neutral red.	...	Fluoresceïn.
Malachite green.	...	Methyl orange.
Brilliant green.	Acid green. (Practically all extracted by boiling water.)	Tropæolin.
Methylene blue.	...	Orange IV.
Bismarck brown.	...	Ponceau 4R.
...	...	Bordeaux R.
Crystal violet.	...	Sudan red.
Methyl violet B extra.	...	Tartrazine.
Auramine.	...	Naphthol yellow.
...	...	Picric acid.
...	...	Naphthol green.
...	...	Indigo carmine.
...	...	Cochineal (1 per cent. solution).

Should therefore a mixture contain, for example, Auramine and Indigo carmine, treatment with kaolin will effect a separation, the Auramine being adsorbed and the Indigo carmine passing into the filtrate.

In some cases, although a dyestuff is readily soluble in alcohol, yet it cannot be dissolved from the coloured kaolin by means of that solvent. By making use of this property, therefore, an approximate separation of three dyestuffs may be effected by washing the coloured kaolin with hot water and then with hot alcohol. The following are examples of separations effected in this manner:—

Ponceau 4R:	Aqueous filtrate.	Red.
Crystal violet:	Alcoholic filtrate.	Purple.
Safranine:	Kaolin.	Pink.
Naphthol yellow:	Aqueous filtrate.	Yellow.
Magenta:	Alcoholic filtrate.	Red.
Methylene blue:	Kaolin.	Purplish-blue.
Fluoresceïn:	Aqueous filtrate.	Dirty pink and fluorescent.
Brilliant green:	Alcoholic filtrate.	Green.
Congo red:	Kaolin.	Pink.

The dyestuffs, after separation, can then be identified by special tests.

CHAPTER XXXIV.

INVESTIGATION OF DYESTUFFS ON THE FIBRE.

The large number of synthetic dyestuffs, and the use of various members of them for the production of different shades, renders any identification of them on the fibre an extremely difficult and sometimes impossible task.

It is impossible, for instance, to determine the exact nature of the various dyestuffs which have been used to produce, say, a black or a green upon the fibre; but it is possible, by studying the reactions on the fibre of the various types of the different dyestuff groups, to obtain a fairly clear insight into the character of the dyestuffs that have been employed, and by these means to reproduce the same colour by the use of other similar dyestuffs of the same groups.

In a few cases only, where a pure dyestuff has been used, can its presence on the fibre be with certainty identified.

In the first place, it is, of course, of importance to determine whether or not the dyestuff has been fixed upon the fibre by the aid of a mordant.

The best method for this purpose is to ignite specimens of the dyed fibre, and then to submit the ash to ordinary qualitative analysis.

Care must be taken, however, that all weighting material, etc., used in the finishing of the fabric has previously been removed. This can usually be effected by thoroughly washing the fibre with hot water, which removes the soluble substances used for this purpose, whilst the metallic salts used as the mordant remain unattacked.

The colour of the ash frequently indicates the nature of the metallic salt used. Thus, with iron mordants the ash is brown; with copper and manganese, yellowish-green or bluish-green; and with tin, aluminium, etc., usually bluish-black; the presence of the metal must, however, always be confirmed by analysis.

Certain substances used in mordanting, such as tannin and oleic acid, being organic, burn away with the fibre, and therefore cannot be identified by this means.

Tannic acid (*tannin*) is usually accompanied by antimony, iron, or tin. It can be detected by extracting different portions of the specimen with (1) hot water, (2) 2 per cent. sodium carbonate solution, (3) 5 per cent. acetic acid; according to the condition in which the tannic acid is present, it will be extracted by one of these reagents, and the neutralised extract will give the characteristic tannin reaction with ferric chloride.

Oleic acid usually accompanies aluminium or similar mordants. It is always present in Turkey-red dyeings, and can be detected by extracting with hot dilute hydrochloric acid, filtering, and extracting the filtrate with ether.

Another method of identifying the mordant on a fibre consists in first destroying the colour with bleaching-powder solution.

This can usually be effected by steeping it for some minutes in a 1 per cent. solution of bleaching-powder, but if this is not sufficient, a stronger solution can be taken and the action of the bleaching-powder accelerated by the addition of

acetic acid; under these conditions the fastest dyestuffs will be destroyed, and the decolorised fibre can be investigated for the presence of the mordant.

Iron and chromium can be detected by the colour, although it should be remembered that the prolonged action of bleaching-powder may convert the chromium oxide into chromium chromate.

Aluminium and tin mordants would leave the fibre colourless; they may be identified by dyeing the decolorised specimen in Alizarine.

Reactions of the more important Dyestuffs on the Fibre.

Indigo.—Fibres dyed with pure Indigo are not extracted either by boiling water or boiling alcohol, and the solution remains colourless. In the same way boiling borax or alum solution should extract no colouring matter.

If the dyed fabric has been after-treated with Logwood, the borax solution will be red; and if with aniline colours, or with Indigo carmine, it will be blue.

If this blue extract is treated with concentrated sulphuric acid, it will be transformed into yellow or red if aniline colours have been present; but remains blue if Indigo carmine has accompanied the Indigo.

If Prussian blue is present in an Indigo dyeing, the fibre will be coloured more or less brown by sodium carbonate solution; and if the sodium carbonate extract is treated with ferric chloride, Prussian blue will be precipitated.

Indigo carmine will also be extracted by sodium carbonate solution, and the solution on acidifying will become deep blue.

On boiling Indigo-dyed material for some time with glacial acetic acid, chloroform, aniline, etc., the dyestuff can be quantitatively extracted and, after evaporating the solvent, weighed.

If the acetic acid solution of Indigo thus extracted be shaken with ether, and then water added, the Indigo will remain at the bottom of the ether layer, and the colour of the aqueous solution will determine the presence of impurities.

If the colour is yellow, vegetable dyestuffs have probably been present; whereas, if it is blue or violet, the presence of synthetic colours would be indicated. Indigo-dyed fibre is decolorised by alkaline hyposulphite or stannous salts, and from the yellow extract, on exposure to the air, Indigo is precipitated.

By carefully heating a portion of fabric dyed with Indigo, a quantity of the colouring matter can be sublimed from it.

This experiment can be quickly and readily carried out by setting fire to a small piece of the dyed fabric and flapping the burning material on to a piece of white paper. If Indigo is present, it will appear on the paper in the form of blue streaks.

Anthracene dyestuffs.—The presence of Alizarine can frequently be detected by treating the dyed fibre with concentrated sulphuric acid and pouring the extract (after dilution) into caustic soda, when the characteristic colour of the alkali salt of the dyestuff becomes apparent.

Many of them can be detected by boiling the sample first, for some time, with dilute hydrochloric acid; then with dilute sodium carbonate; mixing the extracts and neutralising (if necessary) with NaOH. By this means the various colour lakes are precipitated and can in many cases be detected by their colour.

Alizarine red is bleached by *bleaching-powder* solution and by *chromic acid*; boiled with *barium hydroxide* solution it becomes violet; with *nitric acid* or *nitric acid vapour* it gives the characteristic yellow of nitroalizarine.

Alizarine blue is unacted upon by *bleaching-powder*; is changed to yellow, which slowly becomes brown, by *nitric acid*; *phosphoric acid* extracts an orange-red solution, which, on dilution with water and treatment with ammonia, becomes blue.

A characteristic absorption spectra is shown by a dilute solution in alcoholic ammonia.

Aniline black is changed by bleaching-powder to brown-red, is decolorised by prolonged action of a concentrated solution of potassium permanganate and oxalic acid, and is changed to a greenish-black by sulphurous acid.

Basic dyestuffs can, for the most part, be extracted by 90 per cent. alcohol, and can be detected by dyeing tannined cotton in the extract.

Magenta is decolorised by sodium sulphide solution. The presence of Archil and Aurine is determined by extraction with amyl alcohol. Magenta gives with amyl alcohol a blue-red extract; Aurine, yellow; and Archil, a rose-violet. On addition of ammonia, Magenta is decolorised, Archil becomes blue, and Aurine remains unchanged.

Methylene blue.—Fibres dyed with Methylene blue are changed to green by *nitric acid*, the green colour remaining; *bleaching-powder* renders it first green and then colourless. The dyed material is very sensitive towards oxidising agents, and a 3 per cent. solution of *potassium bichromate* converts the blue first into violet and then decolorises it. If the Methylene blue has been dyed on tannin a brown colour remains.

Eosine A (tetrabromofluoresceïn), boiled with *20–40 per cent.* KOH, gives an orange-red solution, which, by longer boiling, becomes purple and finally blue with strong green fluorescence. Colour and fluorescence remain on dilution.

Eosine B (ethyl salt of Eosine A) gives, under similar conditions, a blue-violet solution with green fluorescence.

Eosine BN (dinitrodibromofluoresceïn) gives with KOH an olive-green solution without fluorescence.

Congo red.—Material dyed with Congo red gives a blue-black spot with *nitric acid*, which is reconverted into the original red on treatment with ammonia. *Nitrous acid* renders the fibre red-brown; ammonia does not restore the original colour, but makes the fibre purple-brown and the solution blue-red. *Picric acid* renders the fibre blue-black. (Benzopurpurine is made brown-black by nitrous acid and red-brown by picric acid.)

Primuline red (Primuline + β-naphthol) is converted into yellow on boiling with an alkaline solution of a *stannous salt.* If the yellow fibre thus produced is treated with *nitrous acid* and developed with β-naphthol, the original colour is produced.

Picric acid.—Material dyed with picric acid becomes red on treatment with a solution of *potassium cyanide*, owing to the formation of isopurpuric acid.

Naphthol yellow (Martius yellow) is extracted from the fibre by boiling with water, and is decolorised by sulphuric acid. Boiling *potassium cyanide* solution extracts a red coloration. The fibre, when set on fire and flapped on white paper, gives a yellow streak, owing to the volatilisation of the dyestuff.

Naphthol yellow S is not so readily extracted by water and is non-volatile.

Azo-blue is coloured brown-black by picric acid. *Resorcin green* always contains iron, and its presence can be detected in the ash. *Nitric acid* produces a yellow-brown spot.

Separation of Colouring Matters by means of Amyl Alcohol.

It frequently happens that a mixture of dyestuffs present on the fibre can be detected by means of amyl alcohol.

For this purpose a fairly large specimen of the dyed material should be boiled with sodium carbonate solution (or other suitable solvent), and the coloured solution extracted shaken thoroughly with freshly distilled amyl alcohol.

Certain dyestuffs—as, for instance, some azo-compounds such as Orange II.,

Bordeaux, etc.—are extracted by the amyl alcohol; whilst others—such as Indigo carmine, Fast blue, Induline, etc.—remain in the aqueous solution.

The dyestuffs present in the aqueous solution can then be investigated in the usual way, whilst those present in the amyl alcohol can be recovered by evaporation and also submitted to examination.

The amyl alcohol solution can also be submitted to spectroscopic examination (*Formánek*, *Pokorny*).

Titanous Chloride as a Reagent for Testing Colours on the Fibre.

(Knecht, *Journ. Soc. Dyers and Colorists*, vol. xx., 1904, No. 4.)

Knecht recommends titanous chloride as a reducing agent for testing the nature of colouring matters on the fibre.

Azo-dyes, on cotton, are almost instantly discharged when boiled with a dilute solution of titanous chloride; Primuline red is discharged to a yellow; Para-nitraniline red is discharged white after boiling for about two minutes; whereas α-naphthylamine claret (diazotised α-naphthylamine + β-naphthol) requires a longer time for its destruction. Primuline (undeveloped) and allied colouring matters are not affected even on boiling for some time.

Basic colours.—These colours dyed on the usual tannin and tartar emetic mordant are in most cases completely destroyed, the fibre remaining a dull yellow to brown in consequence of the formation of tannate of titanium. Except in a few cases (Rhodamine, Thioflavine T), the colour is not afterwards restored by washing in running water, or on treatment with dilute hydrogen peroxide, the reduction having gone further than the formation of the leuco-base.

Sulphide or Sulphur colours.—The sulphide colours are readily acted upon by titanous chloride on being boiled in dilute solution; they rapidly lose their characteristic colour and turn brown or drab.

At the same time sulphuretted hydrogen is given off, as in the case with stannous chloride, but more readily than with the latter reagent.

The presence of sulphuretted hydrogen can be readily detected by placing a piece of filter-paper moistened with lead acetate over the mouth of the test-tube in which the fibre is being tested.

In using titanous chloride instead of stannous chloride in this reaction, it should be noted that this reagent frequently evolves traces of sulphuretted hydrogen, the origin of which is not known; hence, before using it for this particular test, it should be first boiled for some time with the addition of a small quantity of strong hydrochloric acid.

The sulphide colours are not permanently destroyed by the action of titanous chloride, and the colour is restored either by washing with water or by immersion in dilute hydrogen peroxide.

Aniline black.—This colour behaves in a very similar way to the sulphide blacks, turning to a brown or drab, which becomes black again on washing in running water or exposure to the air.

It is important to note that most Aniline blacks also give off small quantities of sulphuretted hydrogen. The amount is certainly nothing like that evolved from a sulphide black, but the circumstance must naturally be taken into consideration when discriminating between the two classes of blacks.

Indigo.—This colour is first converted by the action of titanous chloride into Indigo white, and the fabric, if taken out after not too long an immersion and placed in dilute caustic soda, will yield some of its colour to the latter.

But if the material is boiled for more than a few minutes, the reduction goes further than Indigo white and the dyestuff is completely destroyed.

This action of titanous chloride is of considerable importance, since it enables the chemist to easily and rapidly detect the presence of sulphide colours which have been used as a bottom for Indigo, or which may have been used along with Indigo in the vat.

Turkey-red, when heated with titanous chloride, becomes maroon, presumably in consequence of the conversion of the alumina lake into the corresponding titanium lake of Alizarine.

Spectroscopic Investigation of Dyestuffs.

(J. Formánek and E. Grandmougin, *Spektralanalytischer Nachweis künstlicher organischer Farbstoffe*; see also *Zeit. Farb. Ind.*, 1902–1903.)

As far as present investigation goes it would appear as if the spectroscopic examination of the dyestuffs, both in the solid form and upon the fibre, will ultimately constitute the safest and surest method of estimating their character, both as regards the nature of a mixture as well as the probable chemical constitution of a homogeneous dyestuff.

It has been noticed, by comparing the absorption spectra of the various groups of dyestuffs, that the presence of certain atomic groupings produces characteristic spectra, by which the presence of such groups can with confidence be predicted. Thus solutions of triamidotriphenylmethane dyestuffs show two unequal symmetric absorption lines; the Thiazines two unequal asymmetric lines; the solutions of Alizarine dyestuffs three absorption lines; the solutions of the azo-compounds one or two broad absorption bands, and so on.

This method can be applied not only to the solid dyestuffs, but also to the dyestuffs on the fibre.

In this case the solvent used may be either water, absolute alcohol, equal parts of alcohol and water, 90 per cent. acetic acid, or equal parts of aniline and acetic acid—solvents which will be found in most cases effective.

In order to extract the dyestuff from the fibre, it is first boiled with absolute alcohol; if the fibre is not completely decolorised by this means, it is further boiled with acetic acid, and finally, if necessary, with the mixture of aniline and acetic acid.

By this treatment it frequently happens that a mixture of dyestuffs is separated, owing to the different solubility of the various constituents; thus, if a fibre has been dyed with a mixture of Methylene blue and Methyl violet, the whole of the Methyl violet would be extracted by the absolute alcohol, whilst the Methylene blue would only pass into solution when boiled with dilute alcohol, or, better still, with acetic acid.

The solutions obtained by the various solvents are then subjected to spectroscopic examination. If they show similar absorption spectra they are mixed and evaporated to dryness, the residue being subsequently extracted with water, ethyl alcohol, and amyl alcohol, and the solutions obtained again examined by the spectroscope.

It is frequently possible to detect the presence of a mixture by merely examining the solution of a mixed dyestuff by the aid of the spectroscope. This is especially the case in respect to the Triphenylmethane dyestuffs, the Quinoneimide dyestuffs, and the Acridine dyestuffs, the absorption spectra of which are clearly and sharply defined.

The presence of a mixture is usually indicated by the unequal arrangement of the absorption lines. Thus if the spectra shows two clear, well-defined lines on either side of a weaker one, the presence of a mixture can with confidence be suspected.

In cases where the absorption lines of dyestuffs occurring in a mixture mask one another, it is often possible to separate them by means of acids or alkalies.

Thus, in a mixture of Induline and Methyl violet (aqueous solution) the absorption line of the Methyl violet would be covered by that of the Induline. If, however, dilute acid is added to the aqueous solution, the line of the Methyl violet will travel towards the left, and the two lines will be clearly visible.

Amyl alcohol has already been mentioned as a valuable means of separating mixtures of dyestuffs, and it can also be used in connection with their spectroscopic examination, since, after extraction, the amyl alcohol solution can be directly submitted to investigation by the aid of the spectroscope. Thus if a mixture of Nile blue A and Methyl violet is treated with amyl alcohol, the Methyl violet dissolves, leaving the Nile blue unattacked.

The basic dyestuffs fixed on cotton by the aid of tannin and tartar emetic can be investigated in the usual way; if, however, aluminium, iron, chromium, or tin have been used as a mordant, it is advisable to evaporate the acetic acid extract to a small bulk, add water, then carefully extract with amyl alcohol. The amyl alcohol will dissolve the dyestuff, leaving the mordant in the aqueous solution; the two can be separated by means of the separating funnel, and the amyl alcohol solution subjected to spectroscopic examination.

Reactions of Dyestuffs on the Fibre.

A. G. Green,[1] assisted by H. Yeoman and J. R. Jones, has worked out a scheme for the *Identification of Dyestuffs on Animal Fibres* on the principle, with modifications, of his method for the analysis of colouring matters in substance. The scheme also takes into consideration methods for ascertaining the dyeing properties of the dyestuff on the fibre. Such tests (so-called "stripping tests") are an inversion of the respective dyeing process. With regard to the chemical relationship of the dyestuffs, the modifications consist in using sodium hydrosulphite (in place of zinc dust) for the reduction and potassium persulphate (in place of chromic acid) for the re-oxidation of the colouring matter. The leuco-compounds formed by reduction remain in great part attached to the fibre, whilst the splitting products of the azo-dyestuffs can be entirely removed therefrom by washing.

The following is the general behaviour of the various chemical groups of dyestuffs upon animal fibres towards reduction and oxidation :—

Decolorised by Hydrosulphite.			Not altered by Hydrosulphite.	Not decolorised, but changed to Brown. Original colour restored by Air or Persulphate.
Colour restored on Exposure to Air.	Colour not restored by Air, but on Oxidation with Persulphate.	Colour not restored either by Air or Persulphate.		
Azines, Oxazines, Thiazines, Indigo.	Triphenyl-methane group.	Nitro-, Nitroso-, and Azo-groups.	Pyrone, Acridine, Quinoline, and Thiazol groups. Some members of Anthracene group.	Most dyestuffs of the Anthracene group.

[1] *J. Soc. Dyers*, 1905, p. 236.

Having ascertained by means of the Tables both the dyeing group and the chemical relationship of the colouring matter, and taking the shade also into consideration, the question is usually narrowed down to a single representative or to a choice between a limited number of closely related dyestuffs. For distinguishing between these the behaviour with concentrated sulphuric acid or strong hydrochloric acid can be frequently employed. In the appended tables the subdivision of the groups has been usually omitted as unnecessary, but is given in a few instances (see Table II.), in order to illustrate the general method. For confirmation, the sample should be compared both as to shade and reactions with a dyed pattern of the dyestuff to which it is believed to correspond.

In the appended tables all the possible groups of dyestuffs are considered, although in individual instances many would be at once excluded on account of the nature of the material or its shade. In such cases, therefore, the analytical scheme would be much simplified.

Reayents.—The following reagents are employed :—

1. Dilute ammonia (1 : 100).
2. Aqueous alcoholic ammonia. 1 c.c. strong ammonia, 50 c.c. strong alcohol, 50 c.c. water.
3. Acetic acid (5 per cent. solution).
4. Dilute alcohol (1 : 1).
5. Dilute hydrochloric acid (1 : 10).
6. Caustic soda. 10 per cent. solution.
7. Hydrosulphite A. 10 per cent. solution of formaldehyde-sodium hydrosulphite.
8. Hydrosulphite B. Hydrosulphite A, with addition of 1 c.c. of glacial acetic acid per 200 c.c.
9. Potassium persulphate. Cold saturated solution.
10. Sodium acetate. 5 per cent. solution.

Procedure.—The reactions are performed in test-tubes with pieces of the material about $\frac{3}{4}$ inch to 1 inch square, which are covered with about 1 inch to $1\frac{1}{2}$ inches of the reagent. The tests should be carried out exactly as described. In making "stripping tests" the degree of stripping is judged by comparing the depth of shade remaining with that of the original pattern. The colour of the stripping solution is misleading, and can scarcely be relied upon as a guide. It is found advantageous in boiling with dilute acetic acid and dilute ammonia to repeat the extraction, as a better stripping is thereby obtained, and also with acid dyestuffs any staining of the cotton by the first strong extract is avoided. In testing with dilute ammonia or sodium acetate, the piece is placed in a test-tube with a somewhat smaller piece of white, mercerised cotton cloth, and boiled for the time prescribed. If the shade is a pale one the size of the sample should be increased and that of the cotton diminished. The dilute ammonia is replaced by aqueous alcoholic ammonia in the case of the violet and black dyestuffs (Tables III. and VII.), as in these cases the acid dyestuffs are less easily extracted, and the cotton is more liable to be stained by them. In making reduction tests, the sample is boiled for from one-quarter to one minute with the hydrosulphite, then rinsed well under the tap, and allowed to lie on white paper for an hour or so. With most dyestuffs which form air-oxidisable leuco-compounds, the colour returns immediately or in a few minutes, but with others a longer time is required. The reaction is accelerated by exposing the pattern to ammonia vapour. If the colour does not return the pattern is heated to boiling in a test-tube with a little water, and potassium persulphate is added drop by drop, carefully avoiding an excess. If this also fails to cause any return of colour, the dyestuff is to be regarded as an azo-compound. The

depth of the restored colour varies greatly in different cases; whilst with some dyestuffs the colour reappears with nearly its original depth, with others (probably on account of the greater solubility of their leuco-compounds) only a light shade may return. Safranine and its azo-derivatives yield on re-oxidation of the leuco-compound a violet colour. This is due to the condensation of the leuco-safranine with the formaldehyde present in the hydrosulphite NF.

The reactions given in the annexed analytical tables were mostly ascertained upon the wool fibre, but from a number of tests which were also conducted for comparison upon silk, there is no reason to believe that the latter fibre will exhibit any variations in behaviour. On the other hand, cotton and other vegetable fibres require rather different treatment, and are described below.

In a subsequent communication Green[1] (in collaboration with Yeoman, Jones, Stephens, and Haley) describes a systematic method for the *Identification of Dyestuffs on Vegetable Fibres.* In many respects the methods employed differ from those used in detecting dyes on wool and silk, principally on account of the influence exerted by mordants on the properties of the dyestuffs, and also on account of the difference between the affinity of colouring matters for the two types of fibre. Many basic dyestuffs, for instance, which, if dyed on wool, are easily reduced by sodium hydrosulphite, are scarcely affected by this reagent when fixed on tannin-mordanted cotton. Nor can basic dyestuffs so fixed be stripped by acetic acid as they can from the wool fibre. Further, whilst in the case of wool the leuco-compounds of dyestuffs remain in great part attached to the fibre, and can, therefore, be re-oxidised, this is frequently not the case with cotton.

In order to overcome the difficulty introduced by the presence of a tannin mordant, the latter is removed by boiling with caustic soda; and to prevent this reagent from stripping the dyestuff at the same time, the solution is saturated with common salt. The basic dyestuffs are thus left on the fibre in the form of free colour-bases, which can then be readily stripped by boiling with dilute acetic acid, or preferably with dilute formic acid. Although most other colours are unaffected by boiling with the "saline caustic soda," as the above reagent is termed, some mordant dyes, such as Turkey-red, are partially decomposed. In such a case the acetic or formic acid extract will usually not have the colour of the dyed material; but in order to avoid any possibility of error from this cause, if the colour is appreciably stripped a solution of tannin is added to the acid extract, when a coloured precipitate will result if a basic dyestuff is present.

As already mentioned, many basic dyestuffs fixed upon a tannin mordant do not behave normally upon reduction with hydrosulphite, or if the leuco-compound is formed it may pass into solution and thus render reoxidation on the fibre impossible. To overcome this difficulty the dyestuff is transferred to wool, and the tests with hydrosulphite and persulphate made on this fibre instead of upon the original cotton.

A class of dyestuffs which occupy a somewhat intermediate position between the basic colours and the mordant colours, since they contain the characteristic groupings of both classes, are the dyestuffs of the Gallocyanine series and the Chrome colours of the Rosaniline series. These products, when treated with saline caustic soda followed by dilute formic acid, behave like basic dyestuffs, except that they are less completely extracted. The acid extracts, though precipitated by tannin, give a finer and less distinct precipitate. As a means of distinction from ordinary basic dyestuffs, use is made of the fact that they cannot be transferred to wool by the methods applicable in other cases.

[1] *J. Soc. Dyers*, 1907 p. 252.

With colours other than basic and acid dyestuffs, the reduction and oxidation tests are performed on the cotton fibre itself, and in order to accelerate the reduction a small quantity of anthraquinone is added to the hydrosulphite solution. Sulphide colours are identified by the stannous chloride test, carried out in the manner described in the *Journal of the Society of Dyers and Colourists*, 1907, p. 118. Before applying the stannous chloride the fabric is boiled one or two minutes with a 10 per cent. solution of caustic soda. This has the effect of removing free sulphur and most sulphur compounds other than sulphide dyestuffs. It has been found, however, that some "Salt colours" (Direct Cotton Colours) evolve hydrogen sulphide when heated with stannous chloride.

Reagents.—The following reagents are used for colours on vegetable fibres:—

1. Dilute ammonia (1 : 100).
2. Caustic soda, 10 per cent. solution.
3. Saline caustic soda, 10 c.c. of 40 per cent. solution caustic soda to 100 c.c. saturated solution of common salt.
4. Formic acid, 90 per cent.
5. Dilute formic acid (1 : 100).
6. Dilute hydrochloric acid (1 : 20).
7. Soap solution, 2 per cent. solution.
8. Tannin solution, 10 grams, with 10 grams sodium acetate per 100 c.c.
9. Bleaching-powder solution, 5° Tw.
10. Hydrosulphite A, 5 per cent. solution of Rongalite or of Hyraldite C extra or of Hydrosulphite N F conc. (formaldehyde-sodium hydrosulphite).
11. Hydrosulphite B. Hydrosulphite A, with addition of 1 c.c. of glacial acetic acid per 200 c.c.
12. Hydrosulphite X. 50 grams of Rongalite or Hyraldite C extra or Hydrosulphite N F conc. in 125 c.c. of hot water mixed with 1 gram of anthraquinone ground with a little of the Rongalite solution, and the whole heated to 90° C. for one or two minutes, diluted with cold water to 500 c.c., and acidulated with 1·5 c.c. of glacial acetic acid.
13. Potassium persulphate, cold saturated solution (or a 2 per cent. solution of ammonium persulphate).
14. Acid stannous chloride, 10 grams of stannous chloride, 100 c.c. hydrochloric acid (30 per cent.), and 50 c.c. of water.

Procedure.—The reactions are performed in test-tubes, as described for *Animal Fibres* on p. 391. With cotton and wool or cotton and silk unions the weft is separated from the cotton warp and both submitted to examination. Doubt may frequently exist as to how a particular shade should be classified, whether, for instance, a reddish-blue is to be regarded as a blue or a violet. In such cases the table referring to both shades should be employed; since the same general scheme is adopted throughout the tables, this can scarcely give rise to confusion. The same remark applies to possible mixtures; thus in examining a certain green shade, both the yellow and the blue tables may require to be used. To distinguish between individual dyestuffs of the same group, the reactions towards concentrated sulphuric acid, caustic soda, etc., may be employed.

Stripping Test for Acid Colours.—A few salt dyestuffs are partially stripped by weak ammonia, and may thus give rise to the impression that they are acid colours. To avoid this error it is advisable to add a small piece of white cotton when carrying out the test. If the dyestuff is an acid one, the cotton is either not tinted or becomes white on boiling a second time with dilute ammonia.

Transference of Basic Colours to Wool.—The tannin mordant is first removed, as in testing for a basic colour, by boiling the pattern for half a minute with saline caustic soda. It is then well washed to remove all alkali, and is boiled with a piece of white wool half the size of the cotton (or less) in water for one or two minutes. In most cases the dye-base will leave the cotton almost entirely, and dye the wool a full shade. If the colour does not develop on the wool one or two drops of weak formic acid (1 : 100) may be added. In the case of a few dyestuffs which are more difficult to strip (*e.g.*, basic greys) it is necessary to extract the colour with dilute hydrochloric acid (1 : 5), carefully neutralising the extract with ammonia before adding the wool.

Transference of Acid Colours to Wool.—The cotton is simply boiled with a small piece of wool and weak formic acid (1 : 100).

Tannin Test for Basic Colours.—A few drops of tannin solution are shaken with the formic acid extract of the colour. Some colouring matters, such as the Rhodamines, Gallocyanines, and Chrome colours of the Rosaniline series (which contain carboxyl or hydroxyl groups in addition to basic groups) only precipitate slowly, whilst the precipitate being more finely divided is sometimes difficult to see.

Bleeding Test for Salt Dyestuffs.—In testing for salt dyestuffs by the bleeding test, the sample is placed in a test-tube together with a smaller piece of white mercerised cotton cloth, and boiled with soap solution for about a minute. The soap solution may also be replaced by a 5 per cent. solution of sodium carbonate.

Lead Acetate Test for Sulphide Colours.—The sample is just covered with acid stannous chloride solution. The mouth of the test-tube is closed by a cap of filter-paper closely wrapped round it, into the centre of which is placed by means of a glass rod one drop of lead acetate solution. The contents of the test-tube are slowly heated to the boiling-point, when a blackish-brown stain of lead sulphide appears if a sulphide colour is present.

It is important to pay special attention to the cleanliness of the test-tubes employed for this test, as tubes which have been previously used for hydrosulphite reductions acquire a thin invisible deposit of sulphur upon their walls, which on boiling with stannous chloride gives rise to sulphuretted hydrogen and thus may lead to error.

Reduction and Reoxidation Tests.—The reduction with Hydrosulphite X is carried out by boiling the sample with the reagent for from half to two minutes. The azines, thiazines, oxazines, etc., and most of the azo-dyestuffs are fully reduced in about half a minute, but the insoluble azo-colours and some salt dyestuffs require from one to two minutes to complete their reduction. In testing the reoxidisability by air, the reduced sample should be exposed to the fumes from an ammonia bottle, which in many cases accelerates oxidation.

The reactions of the various colouring matters on vegetable fibres are given in Tables I. to VII.

IDENTIFICATION OF DYESTUFFS ON VEGETABLE FIBRE.

TABLE I.—YELLOW AND ORANGE COLOURS.

Boil with Weak ammonia (1:100).

The colour is stripped. Boil with acidified water and small piece of white wool.			The colour is not stripped. Boil for half minute with Saline caustic soda, rinse and boil twice with Weak formic acid (1:100).																
			The colour is completely destroyed, both alkaline and acid solutions and the fibre being colourless. Treat original fibre with cold ammonium sulphide.				The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by Tannin solution:—Basic dyestuff. Transfer to wool and boil with hydrosulphite B.			The colour is not stripped or the acid extract is not precipitated by Tannin solution. Reduce with hydrosulphite X.								
										Decolourised and colour not restored by air or persulphate:—Azo dyestuff (including Stilbene Group). Boil with soap solution and white mercerised cotton.				The colour is unaffected or changed in shade (becoming yellower, browner, or blue). Apply lead acetate test.					
				Fibre is not blackened. Boil with hydrosulphite X.				Wool is not decolourised. Boil cotton with hydrochloric acid (1:20).			White cotton is stained:—Salt Colour. Test ash for Cr and Cu.		White cotton is not stained. Boil with pyridine.		H_2S is evolved. After reduction with hydrosulphite the original colour is rapidly restored by air:—Sulphide dyestuff.	No H_2S is evolved. Boil with soap solution and white mercerised cotton.			
																The white cotton is stained:—Thiazol Salt dyestuff.		The white cotton is not stained:—Mordant or Vat dyestuff.		
Colour not transferred to the wool. *So is present in ash.*	Colour is transferred to the wool:—Acid dyestuff. Boil wool with hydrosulphite B.		Fibre blackened. Cr present in ash.	Not decolourised. Test for Al in ash.		De-colourised.	De-colourised.	Not decolourised. The conc. H_2SO_4 and alcoholic solutions are fluorescent:—Acridine Group.	Wool is permanently decoloured:—Azo Group.	No Cr or Cu present:—Salt Azo-dyestuff untreated.	Cr or Cu present:—Salt Azo-dyestuff after-treated.	Colour is stripped:—Insoluble Azo-Colour.	Colour is not stripped. Cr present in ash:—Azo-Mordant Colour.		The colour after reduction with hydrosulphite can be diazotised and developed red with beta-naphthol.	The colour after reduction cannot be diazotised and developed.	The reduced colour is yellow or brownish-yellow. Al or Cr in ash.	The reduced colour is brown, restored to orange by persulphate.	The reduced colour is blue, restored to yellow on exposure to air.
		Not decolourised:—Pyrone or Quinoline Group.		Al present.	Al absent.															
		Permanently decolourised:—Azo Group.																		
1.—Persian Berries on Tin Mordant.	2.—Quinoline Yellow, Eosine Orange.	3.—Indian Yellow, Orange IV., G, &c.	4.—Chrome Yellow or Chrome Orange (Lead Chromate).	5.—Alizarin Yellow A.	6.—Thioflavine T.	7.—Flavinduline.	8.—Auramine.	9.—Phosphine, Benzoflavine, Acridine Yellow, Acridine Orange, &c.	10.—Chrysoidine, Tannin Orange, Janus Yellow, &c.	11.—Chrysophenine, Chrysamine, Toluylene Yellow & Orange, Stilbene Yellows & Oranges, Benzo, Congo, Diamine, & Dianil Yellows & Oranges, Pyramine Orange, &c.	12.—The preceding Coppered or Chromed.	13.—Metanitraniline Orange or Nitrokoluidine Orange (Formed on Fibre).	14.—Chrome Orange, Alizarin Yellow R, GG, &c., Diamond Flavine, Flavazol, &c.	15.—Immedial, Katigene, Pyrogene, Thiogene, Sulphur, &c., Yellows & Oranges.	16.—Primuline developed with Phenol or with Resorcinol. Cotton Yellow G & R, Oriol Yellow, Dianil Yellow, &c.	17.—Chlorophenine, Chloramine Yellow, Diamine Fast Yellow B, FF, & C, Clayton Yellow, Thiazol Yellow, Thioflavine S, &c., Primuline developed with Hypochlorite.	18.—Persian Berries on Al or Cr Mordants.	19.—Alizarin Orange on Al Mordant.	20.—Flavanthrene.

NOTES.—1. Brilliant Yellow is largely stripped by weak ammonia, but if white cotton is present it will be stained. 2. Sulphide Yellows of the thiazol class, such as Katigene Yellow 2G, Pyrogene Yellow, &c., stain white cotton slightly when boiled in soap.
3. Diamond Flavine, if not fully fixed, may stain cotton from a soap solution.

TABLE II.—RED COLOURS.

Boil with Weak ammonia (1:100).

The colour is stripped:—Acid dyestuff. Transfer to wool and boil with hydrosulphite B.		The colour is not stripped. Boil for half minute with Saline caustic soda, rinse, and boil twice for one minute with Weak formic acid (1:100).													
		The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by Tannin solution:—Basic dyestuff (on tannin or other mordant). Transfer to wool and boil with hydrosulphite A.				The colour is not stripped or the acid extract is not precipitated by Tannin solution. Reduce with hydrosulphite X.									
						Decolourised and colour not restored by air or by persulphate:—Azo Group. Boil with soap solution and white mercerised cotton.				Decolourised. Colour returns on exposure to air:—Azine or Indigo Group. Apply lead acetate test.		Colour changed to greenish-yellow which can be diazotised and developed red with beta-naphthol:—Primuline Azo-Colour.	Colour unaffected or changed in shade (becomes browner &c.):—Anthracene Group. Boil with 90 per cent. formic acid.	
						The white cotton is stained:—Salt dyestuff. Test ash for Cr and Cu.		The white cotton is not stained. Boil with pyridine.					Colour is stripped. Test ash for mordant.	Colour not much affected. Test ash for Cr.
Not decolourised:—Pyrone Group.	Decolourised. Colour not restored by air or persulphate:—Azo Group.	Wool not decolourised:—Pyrone Group.	Wool decolourised. Colour returns on exposure to air:—Azine Group.	Wool decolourised. Colour does not return on exposure to air but is restored by persulphate:—Triphenylmethane Group.	Wool decolourised. Colour not restored by air or by persulphate:—Azo Group.	No Cr or Cu present:—Azo-Salt dyestuff.	Cr or Cu present:—Azo-Salt dyestuff aftertreated.	The colour is stripped:—Insoluble Azo-Colour.	The colour is not stripped. Cr in ash:—Mordant Azo-dyestuff.	H_2S is evolved:—Sulphide dyestuff.	No H_2S evolved. Red vapours formed on heating fibre in dry test-tube.		Al present.	Cr present.
1.—Eosins, Phloxine, Erythrosin, Rose Bengal, &c	2.—Crocein Scarlets, Brilliant Croceins, Fast Reds, &c.	3.—Rhodamines, Rhodines, Irisamine, Acridine Reds, &c.	4.—Safranines, Rhoduline Reds and Pink, Azine Scarlet, Induline Scarlet, Neutral Red, &c.	5.—Magenta, Fuchsine, Isorubine, Cerise, Grenadine, &c.	6.—Janus Red.	7.—Benzopurpurine, Diamine Scarlets, Diamine Reds, Benzo Fast Scarlets, Diazo Brilliant Scarlet, Rosanthrenes, Zambesi Red, Erica, Diamine Rose, Geranine, Rosophenine, &c.	8.—Diamine Fast Red F, &c.	9.—Paranitraniline Red, Alphanaphthylamine Bordeaux, Chloranisidine Pink, Nitroanisidine Pink.	10.—Chrome Red, Brilliant Chrome Red, Chrome Bordeaux, &c.	11.—Thiogene Rubine, &c.	12.—Thio Indigo Red, Thio Indigo Scarlet.	13.—Primuline developed with Beta-naphthol or with R-Salt.	14.—Turkey Red, Alizarin Red, Alizarin Pink, Alizarin Maroon.	15.—Alizarin, Purpurins or Alizarin Maroon on Cr Mordant.

NOTE.—Janus Claret Red does not transfer to wool very easily.

e minute with Weak formic acid (1 : 100).

precipitated by Tannin solution. Reduce with hydrosulphite X.

	Decolourised. Colour returns on exposure to air :— Azine or Indigo Group. Apply lead acetate test.		Colour changed to greenish-yellow which can be diazotised and developed red with beta-naphthol :— Primuline Azo-Colour.	Colour unaffected or shade (becomes brow Anthracene G Boil with 90 per cent.	
	H_2S is evolved :— Sulphide dyestuff.	No H_2S evolved. Red vapours formed on heating fibre in dry test-tube.		Colour is stripped. Test ash for mordant.	Col Tes
				Al present.	C
11.—Thiogene Rubine, &c.					
12.—Thio Indigo Red, Thio Indigo Scarlet.					
13.—Primuline developed with Beta-naphthol or with R-Salt.					
14.—Turkey Red, Alizarin Red, Alizarin Pink, Alizarin Maroon.					

TABLE III.—PURPLE AND VIOLET COLOURS.

Boil with Weak ammonia (1:100).

The colour is stripped:—Acid dyestuff. The colour transferred to wool is decolourised by hydrosulphite A and restored by persulphate:—Triphenylmethane Group.		The colour is not stripped. Boil for half minute with Saline caustic soda, rinse and boil twice for one minute with Weak formic acid (1:100).																
		The colour is completely or largely stripped giving a coloured acid extract, which is precipitated by Tannin solution:—Basic dyestuff (on tannin or other mordant) or Basic Mordant dyestuff. Boil with Saline caustic soda, rinse well, and boil with small piece of white wool and plain water.						The colour is not stripped or the acid extract is not precipitated by Tannin solution. Reduce with hydrosulphite X.										
		The wool is dyed:—Basic dyestuff. Boil wool with hydrosulphite A.				The wool is not dyed. Cr is present in ash:—Basic Mordant dyestuff. Boil cotton with hydrosulphite X.		Decolourised and colour not restored by air or persulphate:—Azo Group or Alizarin on Iron (decolourised slowly). Boil with soap solution and white mercerised cotton.				Decolourised. Colour is restored on exposure to air:—Azine, Oxazine, or Thiazine Group. Apply lead acetate test.		The colour is unaffected or changed in shade:—Pyrone or Anthracene Group (also one or two Sulphide dyestuffs).			
								The white cotton is stained:—Salt dyestuff. Test ash for Cr and Cu.		The white cotton is not stained. Boil with hydrochloric acid (1:20).						The colour is changed to brown. Apply lead acetate test.		
										Colour destroyed, giving yellow solution. Fe present in ash:—Alizarin on Fe Mordant.	The colour is not stripped. Boil with pyridine.		H_2S is evolved:—Sulphide dyestuff.	No H_2S is evolved. Cr is present in Ash:—Mordant Oxazine dyestuff (not falling in Group 7).	The colour is unaffected. Al or Cr present in ash:—Pyrone or Anthracene Mordant Colour.	H_2S is evolved:—Sulphide dyestuff.	No H_2S is evolved. Test ash for Al and Cr.	
The ammoniacal solution is colourless, but becomes blue on acidifying.	The ammoniacal solution is violet.	Not decolourised:—Pyrone Group.	Decolourised. Colour returns on exposure to air:—Azine (oxazine or thiazine) Group.	Decolourised. Colour does not return in air, but is restored by persulphate:—Triphenylmethane Group.	Decolourised. Colour is not restored by air or persulphate:—Azo Group.	Decolourised. Colour returns on exposure to air:—Oxazine Group.	Decolourised only slowly. Colour does not return in air, but is restored by persulphate:—Triphenylmethane Group.	No Cr or Cu present:—Azo-Salt dyestuff.	Cr or Cu present:—Azo-Salt dyestuff after-treated.		The colour is stripped:—Insoluble Azo-Colour.	The colour is not stripped. Cr present in ash:—Mordant Azo-dyestuff.				Al or Cr present:—Anthracene Mordant dyestuff.	Al and Cr absent. Anthracene Vat dyestuff.
1.—Red Shades of Soluble and Alkali Blues.																		
2.—Acid Violets, Formyl Violets, &c.		3.—Anisoline.	4.—Methylene Violet, Rhoduline Violet, Iris Violet, Neutral Violet, Tannin Heliotrope, &c.	5.—Methyl Violets, Ethyl Violet, Benzyl Violet, Crystal Violet, &c.	6.—Janus Claret Red, &c.	7.—Gallocyanine, Gallamine Blue, Prune, &c.	8.—Chrome Violet.	9.—Violets of the Diamine, Benzo, Congo, Hessian, Columbia, Chlorazol, Chlorantine, Diamil, Oxamine, and Rosanthrene Series.	10.—The preceding Coppered or Chromed.	11.—Alizarin Purple.	12.—Benzidine Puce.	13.—Chrome Bordeaux, Chrome Prune, &c.	14.—Thiogene Violet, Katigene Violet, &c.	15.—Gallamine Blue, Gallocyanine, &c.	16.—Gallein, Alizarin Violet, Alizarin Claret, Alizarin Cyclamine, Alizarin on Cr Mordant.	17.—Thiogene Dark Red, &c.	18.—Alizarin Cyanin 3R, Alizarin Bordeaux.	19.—Violanthrene.

NOTE.—Alizarin on chromium becomes rather browner on reduction with hydrosulphite X.

TABLE IV.—BLUE COLOURS.

Boil with Weak ammonia (1:100).

The colour is stripped:—Acid dyestuff (or Prussian Blue).		The colour is not stripped. Boil for half minute with Saline caustic soda, rinse and boil twice with Weak formic acid (1:100).																
		The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by Tannin solution:—Basic dyestuff (on tannin or other mordant) or Basic Mordant dyestuff. Boil with Saline caustic soda, rinse well, and boil with small piece of white wool and plain water.						The colour is not stripped or the acid extract is not precipitated by Tannin solution. Reduce with hydrosulphite X.										
		The wool is dyed:—Basic dyestuff. Boil wool with hydrosulphite A.			The wool is not dyed. Cr present in ash:—Basic Mordant dyestuff. Boil cotton with hydrosulphite X.			Decolourised and colour not restored by air or persulphate:—Azo Group. Boil with soap solution and white mercerised cotton.			Decolourised. Colour is restored on exposure to air:—Azine, Oxazine, Thiazine, or Indigo Group. Apply lead acetate test.			Colour changed to greenish-yellow, which can be diazotised and developed red with beta-naphthol:—Primuline Azo-Colour.	Colour unaffected or changed in shade (becoming darker, browner, &c.):—Anthracene Mordant or Anthracene Vat dyestuff (also Ultramarine). Boil with 90 per cent. formic acid.			
								The white cotton is stained:—Salt dyestuff. Test ash for Cr and Cu.		The white cotton is not stained. Colour is stripped by boiling pyridine:—Insoluble Azo-colour.		No H_2S is evolved:—Heat fibre carefully in dry test-tube.			The colour is stripped. Al in ash. Apply lead acetate test.		The colour is not much affected. Test ash for Cr.	
The extract is colourless, but becomes blue on acidification. Transferred to wool, the blue is decolourised by hydrosulphite A, and restored by persulphate:—Triphenylmethane Group.	The extract is colourless and remains so on acidification. $FeCl_3$ gives a blue precipitate.	Decolourised. Colour returns on exposure to air:—Azine, Oxazine, or Thiazine Group.	Colour changes to red just before being decolourised. Colour returns violet or blue:—Safranine Azo-dyestuff.	Decolourised. Colour does not return on exposure to air, but is restored by persulphate:—Triphenylmethane Group.	Decolourised. Colour returns on exposure to air:—Oxazine Group.	Decolourised slowly. Colour restored only by persulphate:—Triphenylmethane Group.		No Cr or Cu present:—Azo-Salt dyestuff.	Cr or Cu present:—Azo-Salt dyestuff after-treated.		H_2S is evolved:—Sulphide dyestuff.	Violet vapours evolved.	No coloured vapour. Cr in ash:—Mordant Thiazine or Oxazine (not falling in Group 6).		H_2S evolved.	No H_2S evolved:—Alizarin dyestuff on Al.	Cr present in ash:—Alizarin dyestuff on Cr.	Cr absent:—Anthracene Vat dyestuff
1.—Alkali or Soluble Blues.																		
2.—Prussian Blue.		3.—Methylene Blue, New Methylene Blue, Nile Blue, Capri Blue, Indazine, Basle Blue, Metaphenylene Blue, Meldola's Blue, Fast Blue, Cresyl Blue, Rhodulin Blue, Nitroso Blue, &c.	4.—Indoine Blue, Janus Blue, Naphthindone Blue, Diazine Blue, &c.	5.—Victoria Blue, Night Blue, Turquoise Blue, Setocyanine, &c.	6.—Gallocyanine, Celestine Blue, Prune, &c.	7.—Chrome Blue.		8.—Blues of the Diamine, Benzo, Congo, Columbia, Chlorazol, Diamil, Oxamine, Chicago, &c., Series.	9.—The preceding Coppered or Chromed.	10.—Dianisidine Blue.	11.—Blues of the Immedial, Katigene, Thiogene, Pyrogene, Sulphur, &c., Series.	12.—Indigo.	13.—Brilliant Alizarin Blue, Delphine Blue, Gallophenine, &c.	14.—Primuline developed with Naphthylamine Ether.	15.—Ultramarine.	16.—Alizarin Cyanins or Anthracene Blues on Al Mordant.	17.—Alizarin Blue, Alizarin Cyanins, or Anthracene Blues on Cr Mordant.	18.—Indanthrene, Cyananthrene.

NOTE.—Alkali Blue dyed on a tannin and tin mordant is only partly stripped by weak ammonia, the solution being colourless.

TABLE V.—GREEN COLOURS.

Boil with Weak ammonia (1 : 100).

The colour is not stripped. Boil for half minute with Saline caustic soda, rinse and boil twice with Weak formic acid.

The colour is not stripped or the acid extract is not precipitated by Tannin solution. Reduce with hydrosulphite X.

The colour is stripped :— **Acid dyestuff.** The colour transferred to wool is decolourised by hydrosulphite A and restored by persulphate :— **Triphenylmethane Group.**	The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by Tannin solution :— **Basic dyestuff** (on tannin or other mordant) or **Basic Mordant dyestuff.** Boil with saline caustic soda, rinse well, and boil with white wool and plain water.			The wool is not dyed. Cr in ash. Cotton decolourised by hydrosulphite X, the colour not returning in air but restored by persulphate :— Triphenylmethane Group.	Decolourised and colour not restored by air or persulphate :—Azo or Nitroso Group. Boil with soap solution and white mercerised cotton.				Decolourised. Colour returns on exposure to air :— Azine, Oxazine, or Thiazine Group. Apply lead acetate test.		The colour is changed to greenish-yellow, which can be diazotised and developed red with beta-naphthol :— Primuline Azo Group.	The colour is unaffected or changed to red, brown, blue, &c. Test ash for Cr and Ni.						
	The wool is dyed :—Basic dyestuff Boil wool with hydrosulphite A.				The white cotton is stained :— Salt dyestuff. Test ash for Cr and Cu.		The white cotton is not stained. Boil with hydrochloric acid (1 : 20).					The ash contains Cr or Ni :— Anthracene Mordant dyestuff.				No Cr or Ni present in ash :— Anthracene Vat dyestuff.		
	Decolourised. Colour returns on exposure to air :—Azine, Oxazine, or Thiazine Group.	Colour becomes red just before being decolourised. Colour returns violet or green on exposure to air :— Safranine Azo Group.	Decolourised. Colour does not return on exposure to air, but is restored by persulphate :— Triphenylmethane Group.		Cr and Cu absent :— Azo-Salt dyestuff.	Cr or Cu present :— Azo-Salt dyestuff after-treated.	Colour destroyed. Fe is present in the ash :— Nitroso Group.	Not decolourised. Cr is present in the ash :— Mordant Azo-dyestuff.	H_2S is evolved :— Sulphide dyestuff.	No H_2S is evolved :— Mordant Oxazine (or Thiazine.		Reduced colour is brownish-red. Green restored by persulphate but not by air. Boiling HCl (1 : 20) gives bright green solution.	Reduced colour is brown. Green shade returns on exposure to air :— Boil with hydrochloric acid (1 : 20). Colour unaffected. Solution colourless. Cr in ash.	Colour of fibre becomes grey, solution red. Ni in ash.	Colour of fibre rather paler, solution brownish-yellow.	Reduced colour is brownish-olive. H_2S evolved on applying lead acetate test.	Reduced colour is dark maroon. Green shade restored by air.	Reduced colour is blue. Green shade restored by air.
1.—Acid Greens.	2.—Fast Green M, Methylene Green, Azine Green, Capri Green, &c.	3.—Janus Green, Diazine Green, &c.	4.—Brilliant Green, Malachite Green, Methyl Green, Victoria Green. Setoglaucine, &c.	5.—Chrome Green.	6.—Diamine Green, Benzo Green, Columbia Green, Chloramine Green, &c.	7.—The preceding Coppered or Chromed.	8.—Russian Green, Fast Green O, Steam Green, Alsace Green, Gambines, Dioxine, &c.	9.—Diamond Green, &c.	10.—Greens of the Immedial, Katigene, Thiogene, Pyrogene, Sulphur and Thionol Series.	11.—Gallanilo Green, Indalizarine, &c.	12.—Primuline developed with Amidodiphenylamine.	13.—Alizarin Viridine, Brilliant Alizarin Viridine.	14.—Alizarin Green S on Cr Mordant.	15.—Alizarin Green S on Ni Mg Mordant.	16.—Coerulein, Anthracene Green.	17.—Olivanthrene.	18.—Viridanthrene.	19.—Algole Green, Indanthrene in admixture with Flavanthrene.

NOTE.—Greens of the Nitroso Group (Gambines, &c.) may become black on reduction if the hydrosulphite X is insufficiently acid (formation of FeS).

TABLE VI.—BROWN COLOURS.

Boil with Weak ammonia (1 : 100).

The colour is not stripped. Boil for half minute with Saline caustic soda, rinse, and boil twice with Weak formic acid (1 : 100).

The colour is not stripped or the acid extract is not precipitated by Tannin solution.

The colour is stripped :— **Acid dyestuff.** Transferred to wool it is permanently decolourised by hydrosulphite A :— **Azo Group.**	The colour is stripped giving acid extract which is precipitated by Tannin solution :— **Basic dyestuff.** The dyestuff transferred to wool is permanently decolourised by hydrosulphite A:— **Azo Group.**	Decolourised and colour not restored on exposure to air or by persulphate :—**Azo Group** and **Mineral Colours.** Boil with soap solution and white mercerised cotton.				The shade is changed to greenish-yellow which can be diazotised and developed red with beta-naphthol :— **Primuline Azo-Colour.**	Unaltered or changed in shade, becoming darker, paler, yellower, &c. Apply lead acetate test.				
		The white cotton is stained :— Salt dyestuff. Test ash for Cr and Cu.		The white cotton is not stained. Boil with pyridine.			H_2S is evolved :— Sulphide dyestuff.	No H_2S is evolved. Test ash for Cr and Cu.			
		Cr and Cu absent :— Azo-Salt dyestuff.	Cr or Cu present :— Azo-Salt dyestuff after-treated.	The colour is stripped :— Insoluble Azo-Colour. Test ash for Cu.		The colour is not stripped :— Mineral Colour. Treat with sodium bisulphite in the cold.		Cr or Cu (or both) present :—Mordant dyestuff. Boil with HCl (1 : 20).			Cr and Cu absent :— Anthracene Vat dyestuff, &c.
				Cu absent.	Cu present.	Decolourised.	Not decolourised.	Completely stripped.	Not stripped or only slightly. Boil with dilute caustic soda 10 %. Fibre and solution dull violet.	Solution brown, fibre unaffected.	
1.—Fast Brown, Naphthylamine Brown, Acid Brown, &c.	2.—Bismarck Brown, Janus Brown, &c.	3.—Browns of the Diamine, Benzo, Congo, Diaril, Columbia, Hessian, Oxamine and Toluylene Series.	4.—The preceding Coppered or Chromed.	5.—Para Brown (Chrysoidine and Paranitraniline), Benzidine or Tolidine Brown.	6.—Paranitraniline Cutch (Para Red Coppered).	7.—Manganese Bronze.	8.—Iron Buff, Khaki (Oxides of Cr and Fe).	9.—Primuline developed with Metaphenylene Diamine, Terra-Cotta, &c.	10.—Immedial Cutch, Cross Dye Brown, Katigene Browns, Pyrogene Browns, Thiogene Browns, &c.	11.—Anthragallol, Anthracene Brown, Alizarin Brown.	12.—Alizarin Orange on Cr Mordant, Alizarin or Purpurin on Cr.	13.—Cutch.	14.—Fuscanthrene, Paramine Brown (*p*-Phenylene Diamine Oxidised on Fibre).

NOTE.—Iron Buff and Khaki may become black on reduction if the hydrosulphite X is inefficiently acid (formation of FeS).

TABLE VII.—BLACK AND GREY COLOURS.

The colour is stripped :— Acid dyestuff. The dyestuff transferred to wool and boiled with hydrosulphite A is permanently decolourised :— Azo Group.	Boil with Weak ammonia (1 : 100). The colour is not stripped. Boil with Dilute hydrochloric acid (1 : 5). The colour is not stripped (or only slightly). Boil for one minute with Saline caustic soda, rinse, and boil with Dilute hydrochloric acid (1 : 20). The colour is not stripped or acid extract is not precipitated by Tannin solution. Reduce with hydrosulphite X.												
	The colour is stripped.			The colour is largely stripped and the acid extract is precipitated by Tannin solution :—Basic dyestuff. Transfer to wool (see note) and boil with hydrosulphite A.		Decolourised and colour not restored by air or persulphate :—Azo Group. Boil with soap solution and white mercerised cotton.			The colour is unaffected or changed in shade (becoming brown, maroon, &c.).				
						The white cotton is stained. Test ash for Cr. and Cu.		The white cotton is not stained. Colour is stripped by boiling pyridine :— Insoluble Azo-Colour.	The reduced colour is brown but is rapidly restored to black on exposure to air :—Azine, Oxazine, or Thiazine Group. Apply lead acetate test.		The reduced colour is brown. Only slowly and imperfectly restored to black by air but at once by persulphate. Cr present in ash :— Naphthalene Mordant dyestuff.	Colour not changed by reduction (or very slightly) :— Anthracene Group. Test ash for Cr.	
	Fibre and solution colourless.	Solution orange. Fe in ash.	Solution red. Cr in ash.	Decolourised. Colour returns on exposure to air :— Azine, Oxazine, or Thiazine Group.	Colour becomes red just before being decolourised. Violet or violet-blue colour remains in air :— Safranine Azo Group.	Cr and Cu absent :— Azo-Salt dyestuff.	Cr or Cu present :— Azo-Salt dyestuff after-treated.		H_2S is evolved. Fibre becomes colourless or pale buff on boiling with bleaching powder solution 5° Tw. :— Sulphide dyestuff.	No H_2S is evolved. Fibre becomes reddish-brown on boiling with bleaching powder solution 5° Tw. :— An Oxidation Black.		Cr present :— Anthracene Mordant dyestuff.	Cr absent :— Anthracene Vat dyestuff.
1.—Naphthol Blacks, Naphthylamine Blacks, Paraline Black, &c.	2.—Tannate of Iron.	3.—Logwood Black on Iron Mordant.	4.—Logwood Black on Chrome Mordant, Noir Reduit.	5.—Methylene Grey, New Methylene Grey, New Fast Grey, Nigrisine, &c.	6.—Janus Black, Janus Grey, Diazine Grey.	7.—Blacks of the Diamine, Oxydiamine, Benzo, Columbia, Diaml, Pluto, &c., Series, Also Diaminogene, Diazo Blacks, &c. (developed or coupled).	8.—The Preceding Coppered or Chromed.	9.—Azophor Black, &c.	10.—Blacks of the Immedial, Katigene, Cross Dye, Pyrogene, Thiogene, Thionol, Pyrol, Sulphur, &c., Series.	11.—Aged Aniline Black, Prussiate Black, One Bath Aniline Black, Steam Aniline Black, Diphenyl Black.	12.—Naphthazarine S, Alizarin Black S, Alizarin Blue-Black SW, Naphthomelane.	13.—Alizarin Cyanin Black, Alizarin Blue-Black B.	14.—Melanthrene.

NOTE.—Chrome Black (By) becomes light brown on reduction with Hydrosulphite X, and persulphates change the colour to dark brown but not to black.

IDENTIFICATION OF DYESTUFFS ON ANIMAL FIBRE.

TABLE I.—YELLOW AND ORANGE COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.

Much colour is stripped:—Basic dyestuff. Boil with hydrosulphite B.

Not decolourised or only very slightly. Treat fibre with conc. H_2SO_4.

Green fluorescent solution:— **Acridine Group.**

1.—Phosphine, Benzoflavine, Rheonine, Acridine Orange, &c.

Colourless solution. Boil with dilute HCl (1:10).

Completely decolourised.

2.—Auramine.

Fibre and solution pale yellow.

3.—Thioflavine T.

Decolourised. Colour is not restored by air or by persulphate:— **Azo Group.**

4.—Chrysoidine Tannin Orange, Janus Yellow.

Little or no colour is stripped:—Acid, Salt, or Mordant Dyestuff. Boil twice for one minute with dilute ammonia (1:100) and a piece of white cotton. Keep the ammoniacal extract.

Much colour is stripped but cotton remains white:—Acid dyestuff. Boil with hydrosulphite B.

Colour is not affected:— **Quinoline or Pyrone Group.**

5.—Quinoline Yellow, Uranine, Eosine Orange.

Decolourised, and colour does not return on exposure to air or upon oxidation with persulphate:—**Azo Group** or **Nitro Group.** Add conc. HCl to the ammoniacal extract.

No change of colour.

6.—Tartrazine, Oranges G, 2 G, R, &c.

Becomes colourless.

7.—Naphthol Yellow S, Martius Yellow.

Becomes red.

8.—Fast Yellow, Indian Yellow, Azoflavine &c.

Becomes violet or violet red.

9.—Metanil Yellow, Orange IV., Tropaeolin.

Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is tinted (salt dyestuff). Boil with 5 per cent. sodium acetate and white cotton for two or three minutes.

The cotton is stained:—**Salt dyestuff.** Boil with hydrosulphite B.

Not affected or slightly changed in shade:— **Thiazol Group.**

10.—Thioflavine S, Chloramine Yellow, Chlorophenine, Thiazol Yellow, &c., also Turmeric.

Decolourised. Colour restored by exposure to air or more quickly by persulphate:— **Stilbene Group.**

11.—Curcumine S, Mikado Yellows and Oranges, Stilbene Yellows, &c.

Decolourised. Colour not restored by air or by persulphate:— **Azo Group.**

12.—Chrysophenine Benzo, Congo, or Diamine Yellows or Oranges, &c.

The cotton remains white:—**Mordant dyestuff.** Confirm by testing ash for metallic mordants). Boil with hydrosulphite B.

Not affected:— **Flavone** and **Ketone Group.**

13.—Fustic, Quercitron, Weld,* Alizarin, Yellow A, &c.

Colour changed to yellowish-brown:— **Alizarin Group.**

14.—Alizarin Orange.

Decolourised and colour not restored by air or persulphate:— **Azo Group.**

15.—Alizarin Yellows G and R, Anthracene Yellow C, Flavazol, Chrome Orange, &c.

* Weld is partly discharged by acetic acid though the solution remains colourless.

TABLE II.—RED COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.

The colour is stripped:—**Basic dyestuff** or **Soluble Red Woods.** Boil with dilute alcohol (1:1) twice for one minute.

Much of the colour is stripped:— Basic dyestuff. Boil with hydrosulphite A.

Colour not affected.

1.—Basic dyestuff of Pyrone Group.

Colour returns quickly on exposure to air.

Decolourised.

2.—Basic dyestuff of Azine Group.

Colour does not return on exposure to air but is restored by persulphate.

Decolourised.

3.—Basic dyestuff of Triphenylmethane Group.

Colour is not restored either by air or by persulphate.

Decolourised.

4.—Basic Azo dyestuff, *e.g.*, Janus Red.

Unaffected. Al or Cr are present in ash. Boiling with dilute ammonia renders the colour much bluer.

5.—Soluble Red Woods.

Little or no colour is stripped:—Acid, Salt, or Mordant dyestuffs. Boil twice for one minute with dilute ammonia (1:100) and a small piece of white cotton. Keep the ammoniacal extract.

Much colour is stripped but cotton remains white:—Acid dyestuff. Boil with hydrosulphite A.

Colour of wool not altered:—**Pyrone Group.** Acidify the ammoniacal extract.

Precipitation and disappearance of fluorescence.

6.—Eosin, Phloxine, Erythrosine, &c.

No pp. and fluorescence remains.

7.—An Acid Eosin, or Acid Rhodamine.

Decolourised. Colour returns on exposure to air:—**Azine Group.**

8.—Azocarmine or Rosinduline.

Decolourised. Colour does not return on exposure to air but is restored by persulphate:—**Triphenylmethane Group.**

9.—Acid Magenta.

Decolourised. Colour not restored either on exposure to air or on oxidation with persulphate:— **Azo Group.** Boil with dilute bichromate.

Colour unaffected. Evaporate ammoniacal extract and dissolve in conc. H_2SO_4.

Red Solution.

Violet Solution.

Blue Solution.

Green Solution.

Changes to dark maroon or violet black.

10.—Xylidine or Palatine Scarlet. / Crystal Scarlet, Fast Red A, &c. / Crocein Scarlet, Fast Red B, &c. / Biebrich Scarlet, &c. / Chromotropes, Azofuchsine, &c.

Some of the colour is stripped and the wool becomes much bluer. Boil with hydrosulphite A.

Colour slowly changed to dull yellow. Original colour not restored on exposure to air.

11.—Cochineal Scarlet.

Decolourised. Colour is quickly restored on exposure to air.

12.—Archil.

Little or no colour is stripped. The cotton remains white (mordant dyestuffs), or is stained (salt dyestuffs. Boil with 5 per cent. sodium acetate and white cotton for two or three minutes.

The cotton is stained:—**Salt dyestuff.** Test ash for chromium.

Chromium is absent. Treat fibre with conc. sulphuric acid.

Crimson-red Solution.

Violet-red Solution.

Violet Solution.

Blue Solution.

Greenish-blue Solution.

Cr is present. Soluble in conc. H_2SO_4 is Red.

13.—Roscophenine. / Erica or Geranine. / Diamine Scarlet, / Diamine Fast Red. / Hessian Purple. / Anthracene Red.

The cotton remains white:—**Mordant dyestuff.** (Confirm by testing ash for metallic mordants.) Boil with hydrosulphite A.

Colour not affected. Al in ash.

14.—Cochineal Crimson.

Colour slowly changed to yellow or orange. Al in ash.

15.—Alizarin Reds.

Decolourised. Colour is restored by persulphate. Al in ash.

16.—Insoluble Red Woods.

Decolourised. Colour is not restored by persulphate. Cr in ash.

17.—Mordant Azo-Colour.

TABLE III.—PURPLE AND VIOLET COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.

Colour is nearly completely stripped:—Basic dyestuff. Boil with hydrosulphite A.

The colour is not stripped:—Acid, Salt, and Mordant dyestuffs. Boil twice for one minute with aqueous alcoholic ammonia and white cotton.

Much colour is stripped but cotton remains white:—Acid dyestuff. Boil with hydrosulphite A.

Little or no colour is stripped. The cotton remains white (mordant dyestuffs) or is tinted (salt dyestuffs). Boil with sodium acetate and white cotton for two or three minutes.

Decolourised. The colour returns on exposure to air.	Decolourised. The colour only returns on oxidation with persulphate.	Not altered or only partially decolourised:—**Pyrone Group.**	Decolourised. The colour does not return on exposure to air, but is restored upon oxidation with persulphate:—**Triphenylmethane Group.**		Decolourised. The colour returns on exposure to air:—**Azine, Oxazine or Thiazine Group.**	Decolourised. The colour is not restored either by exposure to air or by oxidation with persulphate—**Azo Group.**	**The cotton is stained:—Salt dyestuff.**	The cotton remains white:—**Mordant colour.** (Confirm by testing for metallic mordants in ash.) Boil with hydrosulphite A.				
			The ammoniacal extract is violet or purple.	The ammoniacal extract is colourless, but becomes violet on acidifying. Spot fibre with conc. HCl.				Colour not altered:—**Pyrone Group.**	Colour changed to brown:—**Alizarin Group.** Boil with dilute HCl.		Decolourised. Colour returns on exposure to air.	Decolourised. Colour does not return on exposure to air, but is restored by oxidation with persulphate.	Decolourised. Colour is not restored either by exposure to air or by oxidation with persulphate.
				Becomes green.	No change.				Fibre and Solution yellow.	Fibre and solution red or reddish-brown.			
1.—Basic Violet of the Azine, Oxazine, or Thiazine Groups.	2.—Basic Violet of Triphenylmethane Group, *e.g.*, Methyl Violet.	3.—Fast Acid Violets or Violamines.	4.—Acid Violets, Formyl Violets, &c.	5.—Alkali Violet.	6.—Red Shade of Soluble Blues.	7.—Induline or Fast Blue R, &c.	8.—Lanacyl Violet, Victoria Violet, &c.	9.—Hessian Violet, Diamine Violet, &c.	10.—Gallein.	11.—Alizarin on Fe* or Cr.	12.—Alizarin Bordeaux.	13.—Gallocyanine, Prune, Celestine Blue, &c.	14.—Chrome Violet.	15.—Mordant Azo-Colour.

* Alizarin on iron becomes brown on boiling with 5 per cent. acetic acid.

TABLE IV.—BLUE COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.

Much colour is stripped. Boil with dilute alcohol (1:1) twice for one minute.

Little or no colour is stripped:—Acid, Salt, or Mordant dyestuff. Boil twice for one minute with dilute ammonia (1:100) and small piece of white cotton. Keep the ammoniacal extract.

Much colour is stripped:—Basic dyestuff. Boil with hydrosulphite A.

Much colour is stripped but cotton remains white:—Acid dyestuff. Boil with hydrosulphite A.

Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is tinted (salt dyestuff). Boil with 5 per cent. sodium acetate and white cotton for two or three minutes.

Decolourised. Original colour returns on exposure to air:—**Azine, Oxazine, or Thiazine Group.**	Decolourised. A violet colour returns on exposure to air:—**Safranine Azo-Colour.**	Decolourised. The colour does not return on exposure to air but is restored by persulphate:—**Triphenylmethane Group.**	Unaffected. Al or Cr or both are present in ash. The blue is changed to brick red on spotting with HCl.	Decolourised and colour restored on exposure to air:—**Azine, Oxazine, Thiazine, and Indigo Group.** Also **Prussian Blue.**		Ammon. extract is colourless. Fe in ash.	Decolourised. Colour does not return on exposure to air but is restored by persulphate:—**Triphenylmethane Group.**		Ammon. extract is colourless but becomes blue on acidifying.	Decolourised. Colour is not restored either by air or by persulphate:—**Azo Group.**	Not Decolourised but changed to bluish-red:—**Alizarin Group.**	The cotton is stained **Salt dyestuff.** On reduction with hydrosulphite A the colour is not restored either by air or persulphate:—**Azo Group.**	Blue solution which on evaporation to dryness leaves a residue which sublimes in violet vapours on heating.	The cotton remains white. Boil with a little aniline oil.					
				Ammon. extract is blue, and on adding NaOH			Ammon. extract is blue. On boiling with NaOH it becomes							The solution is light brown or colourless:—**Mordant dyestuff.** Confirm by testing ash for metallic mordants. Boil with hydrosulphite A.				
				at once becomes yellow.	becomes violet on heating.		colourless.	violet.					Colour of wool unaltered:—**Alizarin Group.**	Colour changed to dark brown becoming blue again on exposure to air:—**Alizarin Group.**	Decolourised. But colour returns on exposure to air:—**Oxazine or Thiazine Group.** Treat fibre with conc. H_2SO_4.		Decolourised. Colour does not return on exposure to air, but is restored by persulphate:—**Triphenylmethane Group.**	Decolourised. Colour is not restored either by air or persulphate:—**Azo Group.**
															Green Solution.	Violet Solution.		
1.—Methylene Blue, Nile Blue, Capri Blue, &c.	2.—Indoine, Janus Blue, Naphthindone, Diazine Blue, &c.	3.—Victoria Blue, Night Blue, &c.	4.—Logwood Blue.	5.—Indigo Extract.	6.—Thiocarmine.	7.—Prussian Blue.	8.—A "Wool" Blue.	9.—A "Patent" Blue.	10.—A "Soluble" or "Alkali" Blue.	11.—An Acid Azo-Blue, *e.g.*, Lanacyl Blue.	12.—Alizarin Saphirole, Alizarin Astrole, &c.	13.—Diamine or Benzo Blues, &c.	14.—Indigo.	15.—An Alizarin Cyanin, or Anthracene Blue.	16.—An Alizarin Blue (anthraquinone-quinoline).	17.—Brilliant Alizarin Blue.	18.—Gallocyanines, Celestine Blue, &c.	19.—Chrome Blue.	20.—A Mordant Azo-Blue.

TABLE V.—GREEN COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.

The colour is stripped:—**Basic dyestuff.** Boil with hydrosulphite A.			The colour is not stripped:—**Acid, Salt, or Mordant dyestuff.** Boil twice for one minute with dilute ammonia (1:100) and a small piece of white cotton.								
			Much colour is stripped but the cotton remains white:—**Acid dyestuff.** Boil with hydrosulphite A.			Little or no colour is stripped. The cotton remains white (mordant dyestuff) or is stained (salt dyestuff). Boil for two or three minutes with 5 per cent. sodium acetate and a piece of white cotton.					
							The cotton remains white*:—**Mordant dyestuff.** Confirm by testing for metallic mordant in ash. Boil with hydrosulphite A.				
							Colour changes to brown:—**Alizarin Group.**		Decolourised (or changed to light buff).		
Decolourised. A dark violet colour returns on exposure to air:—Safranine Azo-Colour.	Decolourised. Original colour returns on exposure to air:—**Azine, Oxazine, or Thiazine Group.**	Decolourised. The colour does not return on exposure to air, but is restored by persulphate:—**Triphenylmethane Group.**	Decolourised. Colour returns on exposure to air:—**Azine, Oxazine, or Thiazine Group.**	Decolourised. Colour does not return on exposure to air but is restored by persulphate:—**Triphenylmethane Group.**	Decolourised. Colour is not restored either by air or persulphate:—**Azo Group.**	The cotton is deeply stained:—**Salt dyestuff.**	Original colour returns on exposure to air.	Original colour does not return on exposure to air, but is restored by persulphate.	Colour returns on exposure to air:—**Oxazine or Thiazine Group.**	Colour does not return on exposure to air or upon oxidation with persulphate:—**Nitroso or Azo Group.** Boil with conc. hydrochloric acid.	
										Fibre and solution light brown:—**Nitroso Group.**	Fibre blue and solution colourless:—**Azo Group.**
1.—Janus Green or Diazine Green.	2.—Fast Green M, Azine Green, Capri Green, &c.	3.—Malachite Green, Brilliant Green, Setoglaucine, &c.	4.—Azine Green S.	5.—Acid Greens, Light Green, Guinea Green, Wool Green, &c.	6.—Chiefly Mixtures of an Azo-Blue and Yellow.	7.—Diamine Green, Columbia Green, Chloramine Green, &c.	8.—Coeruleïn or Alizarin Green S.	9.—Alizarin Cyanin Green or Alizarin Viridin.	10.—Alizarin Green G or B.	11.—Gambines, Diozine, Dark Green, Naphthol Green.	12.—Diamond Green, Chrome Patent Green, &c.

* With azo mordant colours the cotton may be slightly tinted, especially if the fixation by chrome is not complete.

TABLE VI.—BROWN COLOURS.

Boil twice for one minute with 5 per cent. acetic acid.

Much colour is stripped:—**Basic dyestuff.** On boiling with hydrosulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate:—**Azo Group.**	Little or no colour is stripped:—**Acid, Salt, or Mordant dyestuff.** Boil twice for one minute with dilute ammonia.						
	Much colour is stripped:—**Acid dyestuff.** On boiling with hydrosulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate:—**Azo Group.**	Little or no colour is stripped:—**Salt** or **Mordant dyestuff.** Boil for two or three minutes with 5 per cent. sodium acetate and white cotton.					
		The cotton is stained:—**Salt dyestuff.** Boil with hydrosulphite A.		The cotton remains white:—**Mordant dyestuff.** Confirm by testing for metallic mordants in ash. Boil with hydrosulphite A.			
		Decolourised, but colour not restored by air or persulphate:—**Azo Group.** Test ash for chromium to ascertain if chromed (Cloth Brown, Chrome Brown, &c.).	Decolourised, but colour returns slowly on exposure to air or quickly on oxidation with persulphate:—**Stilbene Group.**	Colour not changed. Boil with dilute hydrochloric acid (1:10).		Decolourised or changed to pale buff or light brown.	
				Colour is stripped.	Colour not stripped.	Colour returns slowly on exposure to air or quickly on oxidation with persulphate.	Colour not restored either by air or persulphate:—**Azo Group.**
1.—Bismarck Brown.	2.—Acid Brown R, Fast Brown O, &c.	3.—Diamine Browns, Benzo Browns, Toluylene Browns, &c.	4.—Mikado Browns.	5.—Anthragallol (Anthracene Brown).	6.—Cutch.	7.—Chromogen.	8.—Anthracene Acid Browns, Acid Anthracene Brown, Palatine Chrome Brown, &c., also Manganese Brown (Mn in Ash).

TABLE VII.—BLACK AND GREY COLOURS.

Boil twice for one minute with 5 per cent. acetic acid

Much colour is stripped:—**Basic dyestuff.** (N.B.—Logwood black on Fe mordant also becomes much paler though solution is not coloured.)	The colour is not stripped:—**Acid, Salt, or Mordant dyestuff.** Boil twice for one minute with aqueous alcoholic ammonia and small piece of white cotton.										
	Much colour is stripped but the cotton remains white:—**Acid dyestuff.** On boiling with hydrosulphite A the colour is permanently discharged.	The colour is not stripped:—**Salt** and **Mordant dyestuffs.** Boil with 5 per cent. sodium acetate and small piece of white cotton.									
		The cotton is stained:—**Salt** and **Azo Mordant dyestuff.** Permanently decolourised by hydrosulphite A. Test ash for chromium.		The cotton remains white:—**Mordant dyestuffs.** (Confirm by testing ash for mordant). Boil with dilute hydrochloric acid (1:10).							
		Cr is absent:—**Salt dyestuffs.**	Cr is present:—**Mordant Azo dyestuffs.**	Fibre blue and solution crimson. Test for indigo by boiling with a little aniline: blue solution, which on evaporation to dryness gives residue subliming in violet vapour.	Fibre and solution crimson.	Fibre and solution pale brown.	Not affected. Boil with hydrosulphite A.				
							Becomes brown. Original colour slowly returns on exposure to air.	Decolourised. Colour is not restored by exposure to air or by persulphate.	Unaffected. Treat fibre with conc. H_2SO_4.		
									Blue solution.	Colourless solution.	
1.—Diazine Black, Janus Black, Methylene Grey, &c.	2.—Naphthol Black, Naphthylamine Black, Palatine Black, &c.	3.—Union Black, Half-Wool Black, Columbia Black, &c.	4.—Anthracene Chrome Blacks, Palatine Chrome Black, Chromotropes, &c.	5.—A "Vatted Black" (indigo and logwood).	6.—Logwood on Cr.	7.—Logwood on Fe.	8.—Naphthazarine, Alizarin Black S, Alizarin Blue Black SW.	9.—Diamond Blacks.	10.—Alizarin Cyanin Black.	11.—Aniline Black.	

APPENDIX.

TABLES, Etc.

International Atomic Weights, 1918.

		O=16.			O=16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·005	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·0
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·1	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	4·00	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·4
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	118·7
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·2
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·20	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	173·5
Lutecium	Lu	175·0	Yttrium	Yt	88·7
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

Acetic Acid.

Acetic acid (both the dilute acid, 30 to 40 per cent., and glacial acetic acid) is tested by titration with normal caustic soda solution using phenolphthaleïn as indicator.

The specific gravity of acetic acid is shown in the following table (*Roscoe*) :—

Sp. Gr. at 15°.	Acetic Acid, per cent.	Sp. Gr. at 15°.	Acetic Acid, per cent.
1·0007	1	1·0746	75
1·0067	5	1·0748	80
1·0142	10	1·0739	85
1·0214	15	1·0713	90
1·0284	20	1·0705	91
1·0350	25	1·0696	92
1·0412	30	1·0680	93
1·0470	35	1·0674	94
1·0523	40	1·0660	95
1·0571	45	1·0644	96
1·0615	50	1·0625	97
1·0653	55	1·0604	98
1·0685	60	1·0580	99
1·0712	65	1·0553	100
1·0733	70		

Table of Percentages of Hydrochloric Acid.

Specific Gravity.	Degree Baumé.	Degree Twaddell.	Percentage HCl.	Specific Gravity.	Degree Baumé.	Degree Twaddell.	Percentage HCl.
1·000	0·0	0	0·016	1·105	13·6	21	20·97
1·005	0·7	1	0·15	1·110	14·2	22	21·92
1·010	1·4	2	2·14	1·115	14·9	23	22·86
1·015	2·1	3	3·12	1·120	15·4	24	23·82
1·020	2·7	4	4·13	1·125	16·0	25	24·78
1·025	3·4	5	5·15	1·130	16·5	26	25·75
1·030	4·1	6	6·15	1·135	17·1	27	26·70
1·035	4·7	7	7·15	1·140	17·7	28	27·66
1·040	5·4	8	8·16	1·145	18·3	29	28·61
1·045	6·0	9	9·16	1·150	18·8	30	29·57
1·050	6·7	10	10·17	1·155	19·3	31	30·55
1·055	7·4	11	11·18	1·160	19·8	32	31·52
1·060	8·0	12	12·19	1·165	20·3	33	32·49
1·065	8·7	13	13·19	1·170	20·9	34	33·46
1·070	9·4	14	14·17	1·175	21·4	35	34·42
1·075	10·0	15	15·16	1·180	22·0	36	35·39
1·080	10·6	16	16·15	1·185	22·5	37	36·31
1·085	11·2	17	17·13	1·190	23·0	38	37·23
1·090	11·9	18	18·11	1·195	23·5	39	38·16
1·095	12·4	19	19·06	1·200	24·0	40	39·11
1·100	13·0	20	20·01				

Table of Percentages of Nitric Acid at 15°.

Specific Gravity.	Degree Baumé.	Degree Twaddell.	Percentage HNO_3.	Specific Gravity.	Degree Baumé.	Degree Twaddell.	Percentage HNO_3.
1·000	0	0	0·10	1·265	30·2	53	42·10
1·005	0·7	1	1·00	1·270	30·6	54	42·87
1·010	1·4	2	1·90	1·275	31·1	55	43·64
1·015	2·1	3	2·80	1·280	31·5	56	44·41
1·020	2·7	4	3·70	1·285	32·0	57	45·18
1·025	3·4	5	4·60	1·290	32·4	58	45·95
1·030	4·1	6	5·50	1·295	32·8	59	46·72
1·035	4·7	7	6·38	1·300	33·3	60	47·49
1·040	5·4	8	7·26	1·305	33·7	61	48·26
1·045	6·0	9	8·13	1·310	34·2	62	49·07
1·050	6·7	10	8·99	1·315	34·6	63	49·89
1·055	7·4	11	9·84	1·320	35·0	64	50·71
1·060	8·0	12	10·68	1·325	35·4	65	51·53
1·065	8·7	13	11·51	1·330	35·8	66	52·37
1·070	9·4	14	12·33	1·335	36·2	67	53·22
1·075	10·0	15	13·15	1·340	36·6	68	54·07
1·080	10·6	16	13·95	1·345	37·0	69	54·93
1·085	11·2	17	14·74	1·350	37·4	70	55·79
1·090	11·9	18	15·53	1·355	37·8	71	56·66
1·095	12·4	19	16·32	1·360	38·2	72	57·57
1·100	13·0	20	17·11	1·365	38·6	73	58·48
1·105	13·6	21	17·89	1·370	39·0	74	59·39
1·110	14·2	22	18·67	1·375	39·4	75	60·30
1·115	14·9	23	19·45	1·380	39·8	76	61·27
1·120	15·4	24	20·23	1·385	40·1	77	62·24
1·125	16·0	25	21·00	1·390	40·5	78	63·23
1·130	16·5	26	21·77	1·395	40·8	79	64·25
1·135	17·1	27	22·54	1·400	41·2	80	65·30
1·140	17·7	28	23·31	1·405	41·6	81	66·40
1·145	18·3	29	24·08	1·410	42·0	82	67·50
1·150	18·8	30	24·84	1·415	42·3	83	68·63
1·155	19·3	31	25·60	1·420	42·7	84	69·80
1·160	19·8	32	26·36	1·425	43·1	85	70·98
1·165	20·3	33	27·12	1·430	43·4	86	72·17
1·170	20·9	34	27·88	1·435	43·8	87	73·39
1·175	21·4	35	28·63	1·440	44·1	88	74·68
1·180	22·0	36	29·38	1·445	44·4	89	75·98
1·185	22·5	37	30·13	1 450	44·8	90	77·28
1·190	23·0	38	30·88	1·455	45·1	91	78·60
1·195	23·5	39	31·62	1·460	45·4	92	79·98
1·200	24·0	40	32·36	1·465	45·8	93	81·42
1·205	24·5	41	33·09	1·470	46·1	94	82·90
1·210	25·0	42	33·82	1·475	46·4	95	84·45
1·215	25·5	43	34·55	1·480	46·8	96	86·05
1·220	26·0	44	35·28	1·485	47·1	97	87·70
1·225	26·4	45	36·03	1·490	47·4	98	89·60
1·230	26·9	46	36·78	1·495	47·8	99	91·60
1·235	27·4	47	37·53	1·500	48·1	100	94·09
1·240	27·9	48	38·29	1·505	48·4	101	96·39
1·245	28·4	49	39·05	1·510	48·7	102	98·10
1·250	28·8	50	39·82	1·515	49·0	103	99·07
1·255	29·3	51	40·58	1·520	49·4	104	99·67
1·260	29·7	52	41·34				

Table of Percentages of Caustic Soda (Sodium Hydrate).

Specific Gravity.	Degree Baumé.	Degree Twaddell.	Percentage NaOH.
1·007	1	1·4	0·61
1·014	2	2·8	1·20
1·022	3	4·4	2·00
1·029	4	5·8	2·71
1·036	5	7·2	3·35
1·045	6	9·0	4·00
1·052	7	10·4	4·26
1·060	8	12·0	5·29
1·067	9	13·4	5·87
1·075	10	15·0	6·55
1·083	11	16·6	7·31
1·091	12	18·2	8·00
1·100	13	20·0	8·68
1·108	14	21·6	9·42
1·116	15	23·2	10·06
1·125	16	25·0	10·97
1·134	17	26·8	11·84
1·142	18	28·4	12·64
1·152	19	30·4	13·55
1·162	20	32·4	14·37
1·171	21	34·2	15·13
1·180	22	36·0	15·91
1·190	23	38·0	16·77
1·200	24	40·0	17·67
1·210	25	42·0	18·58
1·220	26	44·0	19·58
1·231	27	46·2	20·59
1·241	28	48·2	21·42
1·252	29	50·4	22·64
1·263	30	52·6	23·67
1·274	31	54·8	24·81
1·285	32	57·0	25·80
1·297	33	59·4	26·83
1·308	34	61·6	27·80
1·320	35	64·0	28·83
1·332	36	66·4	29·93
1·345	37	69·0	31·22
1·357	38	71·4	32·47
1·370	39	74·0	33·69
1·383	40	76·6	34·96
1·397	41	79·4	36·25
1·410	42	82·0	37·47
1·424	43	84·8	38·80
1·438	44	87·6	39·99
1·453	45	90·6	41·41
1·468	46	93·6	42·83
1·483	47	96·6	44·38
1·498	48	99·6	46·15
1·514	49	102·8	47·60
1·530	50	106·0	49·02

Table of Percentage of Sulphuric Acid (*Lunge* and *Isler*).

Specific Gravity at $\frac{15°}{4°}$.	Degree Baumé.	Percentage H_2SO_4.	Specific Gravity at $\frac{15°}{4°}$.	Degree Baumé.	Percentage H_2SO_4.
1·000	0	0·09	1·560	51·8	65·08
1·010	1·4	1·57	1·570	52·4	65·90
1·020	2·7	3·03	1·580	53·0	66·71
1·030	4·1	4·49	1·590	53·6	67·59
1·040	5·4	5·96	1·600	54·1	68·51
1·050	6·7	7·37	1·610	54·7	69·43
1·060	8·0	8·77	1·620	55·2	70·32
1·070	9·4	10·19	1·630	55·8	71·16
1·080	10·6	11·60	1·640	56·3	71·99
1·090	11·9	12·99	1·650	56·9	72·82
1·100	13·0	14·35	1·660	57·4	73·64
1·110	14·2	15·71	1·670	57·9	74·51
1·120	15·4	17·01	1·680	58·4	75·42
1·130	16·5	18·31	1·690	58·9	76·30
1·140	17·7	19·61	1·700	59·5	77·17
1·150	18·8	20·91	1·710	60·0	78·04
1·160	19·8	22·19	1·720	60·4	78·92
1·170	20·9	23·47	1·730	60·9	79·80
1·180	22·0	24·76	1·740	61·4	80·68
1·190	23·0	26·04	1·750	61·8	81·56
1·200	24·0	27·32	1·760	62·3	82·44
1·210	25·0	28·58	1·770	62·8	83·32
1·220	26·0	29·84	1·780	63·2	84·50
1·230	26·9	31·11	1·790	63·7	85·70
1·240	27·9	32·28	1·800	64·2	86·90
1·250	28·8	33·43	1·810	64·6	88·30
1·260	29·7	34·57	1·820	65·0	90·05
1·270	30·6	35·71	1·821	...	90·20
1·280	31·5	36·87	1·822	65·1	90·40
1·290	32·4	38·03	1·823	...	90·60
1·300	33·3	39·19	1·824	65·2	90·80
1·310	34·2	40·35	1·825	...	91·00
1·320	35·0	41·50	1·826	65·3	91·25
1·330	35·8	42·66	1·827	...	91·50
1·340	36·6	43·74	1·828	65·4	91·70
1·350	37·4	44·82	1·829	...	91·90
1·360	38·2	45·88	1·830	...	92·10
1·370	39·0	46·94	1·831	65·5	92·30
1·380	39·8	48·00	1·832	...	92·52
1·390	40·5	49·06	1·833	65·6	92·75
1·400	41·2	50·11	1·834	...	93·05
1·410	42·0	51·15	1·835	65·7	93·43
1·420	42·7	52·15	1·836	...	93·80
1·430	43·4	53·11	1·837	...	94·20
1·440	44·1	54·07	1·838	65·8	94·60
1·450	44·8	55·03	1·839	...	95·00
1·460	45·4	55·97	1·840	65·9	95·60
1·470	46·1	56·90	1·8405	...	95·95
1·480	46·8	57·83	1·8410	...	97·00
1·490	47·4	58·74	1·8415	...	97·70
1·500	48·1	59·70	1·8410	...	98·20
1·510	48·7	60·65	1·8405	...	98·70
1·520	49·4	61·59	1·8400	...	99·20
1·530	50·0	62·53	1·8395	...	99·45
1·540	50·6	63·43	1·8390	...	99·70
1·550	51·2	64·26	1·8385	...	99·95

Table of Percentage of Aqueous Ammonia Solution at 15°

(*Lunge* and *Wiernick*).

The numbers given in the third column are corrections to be applied for the interval of temperature 13° to 17°. If, for example, the specific gravity has been found to be 0·900 at 13°, the value at 15° is found by subtracting $2 \times 0{\cdot}00057 = 0{\cdot}001$ from this number (0·900). One obtains the value 0·899, and therefore the percentage of ammonia is ½ per cent. higher.

Specific Gravity.	Percentage NH_3.	Correction for ± 1°.	Specific Gravity.	Percentage NH_3.	Correction for ± 1°.
1·000	0·00	0·00018	0·940	15·63	0·00039
0·998	0·45	0·00018	0·938	16·22	0·00040
0·996	0·91	0·00019	0·936	16·82	0·00041
0·994	1·37	0·00019	0·934	17·42	0·00041
0·992	1·84	0·00020	0·932	18·03	0·00042
0·990	2·31	0·00020	0·930	18·64	0·00042
0·988	2·80	0·00021	0·928	19·25	0·00043
0·986	3·30	0·00022	0·926	19·87	0·00044
0·984	3·80	0·00022	0·924	20·49	0·00045
0·982	4·30	0·00022	0·922	21·12	0·00046
0·980	4·80	0·00023	0·920	21·75	0·00047
0·978	5·30	0·00023	0·918	22·39	0·00048
0·976	5·80	0·00024	0·916	23·03	0·00049
0·974	6·30	0·00024	0·914	23·68	0·00050
0·972	6·80	0·00025	0·912	24·33	0·00051
0·970	7·31	0·00025	0·910	24·99	0·00052
0·968	7·82	0·00026	0·908	25·65	0·00053
0·966	8·33	0·00026	0·906	26·31	0·00054
0·964	8·84	0·00027	0·904	26·98	0·00055
0·962	9·35	0·00028	0·902	27·65	0·00056
0·960	9·91	0·00029	0·900	28·33	0·00057
0·958	10·47	0·00030	0·898	29·01	0·00058
0·956	11·03	0·00031	0·896	29·69	0·00059
0·954	11·60	0·00032	0·894	30·37	0·00060
0·952	12·17	0·00033	0·892	31·05	0·00060
0·950	12·74	0·00034	0·890	31·75	0·00061
0·948	13·31	0·00035	0·888	32·50	0·00062
0·946	13·88	0·00036	0·886	33·25	0·00063
0·944	14·46	0·00037	0·884	34·10	0·00064
0·942	15·04	0·00038	0·882	34·95	0·00065

Specific Gravity of Solutions of Tannic Acid at 15°

(*Trammer*).

Specific Gravity.	Percentage Tannic Acid.	Specific Gravity.	Percentage Tannic Acid.	Specific Gravity.	Percentage Tannic Acid.
1·0040	1·0	1·0092	2·3	1·0144	3·6
1·0044	1·1	1·0096	2·4	1·0148	3·7
1·0048	1·2	1·0100	2·5	1·0152	3·8
1·0052	1·3	1·0104	2·6	1·0160	4·0
1·0056	1·4	1·0108	2·7	1·0164	4·1
1·0060	1·5	1·0112	2·8	1·0168	4·2
1·0064	1·6	1·0116	2·9	1·0172	4·3
1·0068	1·7	1·0120	3·0	1·0180	4·5
1·0072	1·8	1·0124	3·1	1·0184	4·6
1·0076	1·9	1·0128	3·2	1·0188	4·7
1·0080	2·0	1·0132	3·3	1·0192	4·8
1·0084	2·1	1·0136	3·4	1·0196	4·9
1·0088	2·2	1·0140	3·5	1·0200	5·0
1·0242	6	1·0489	12	1·0740	18
1·0324	8	1·0572	14	1·0824	20
1·0406	10	1·0656	16		

Specific Gravity of Solutions of Sodium Carbonate at 15°

(*Lunge*).

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	Percentage by Weight.	
			Na_2CO_3.	Na_2CO_3+10Aq.
1·007	1	1·4	0·67	1·807
1·014	2	2·8	1·33	3·587
1·022	3	4·4	2·09	5·637
1·029	4	5·8	2·76	7·444
1·036	5	7·2	3·43	9·251
1·045	6	9·0	4·29	11·570
1·052	7	10·4	4·94	13·323
1·060	8	12·0	5·71	15·400
1·067	9	13·4	6·37	17·180
1·075	10	15·0	7·12	19·203
1·083	11	16·6	7·88	21·252
1·091	12	18·2	8·62	23·248
1·100	13	20·0	9·43	25·432
1·108	14	21·6	10·19	27·482
1·116	15	23·2	10·95	29·532
1·125	16	25·0	11·81	31·851
1·134	17	26·8	12·61	34·009
1·142	18	28·4	13·16	35·493
1·152	19	30·4	14·24	38·405

Specific Gravity of Solutions of Common Salt at 15° (*Gerlach*)

Specific Gravity.	Percentage NaCl.	Specific Gravity.	Percentage. NaCl.	Specific Gravity.	Percentage NaCl.
1·00725	1	1·07335	10	1·14315	19
1·01450	2	1·08097	11	1·15107	20
1·02174	3	1·08859	12	1·15931	21
1·02899	4	1·09622	13	1·16755	22
1·03624	5	1·10384	14	1·17580	23
1·04366	6	1·11146	15	1·18404	24
1·05108	7	1·11938	16	1·19228	25
1·05851	8	1·12730	17	1·20098	26
1·06593	9	1·13523	18	1·20433	26·395

Specific Gravity of Solutions of Sodium Sulphate (Glauber's Salt) at 19° (*Schiff*).

Specific Gravity.	Percentage Na_2SO_4+10Aq.	Percentage Na_2SO_4.	Specific Gravity.	Percentage Na_2SO_4+10Aq.	Percentage Na_2SO_4.
1·0040	1	0·441	1·0642	16	7·056
1·0079	2	0·881	1·0683	17	7·497
1·0118	3	1·323	1·0725	18	7·938
1·0158	4	1·764	1·0766	19	8·379
1·0198	5	2·205	1·0807	20	8·820
1·0238	6	2·645	1·0849	21	9·261
1·0278	7	3·087	1·0890	22	9·702
1·0318	8	3·528	1·0931	23	10·143
1·0358	9	3·969	1·0973	24	10·584
1·0398	10	4·410	1·1015	25	11·025
1·0439	11	4·851	1·1057	26	11·466
1·0479	12	5·292	1·1100	27	11·907
1·0520	13	5·373	1·1142	28	12·348
1·0560	14	6·174	1·1184	29	12·789
1·0601	15	6·615	1·1226	30	13·230

Specific Gravity of Solutions of Sodium Bisulphite at 15°.

Specific Gravity.	Percentage $NaHSO_3$.	Percentage SO_2.
1·008	1·6	0·4
1·022	2·1	1·3
1·038	3·6	2·2
1·052	5·1	3·1
1·068	6·5	3·9
1·084	8·0	4·8
1·100	9·5	5·7
1·116	11·2	6·8
1·134	12·8	7·8
1·152	14·6	9·0
1·171	16·5	10·2
1·190	18·5	11·5
1·210	20·9	12·9
1·230	23·5	14·5
1·252	25·9	15·9
1·275	28·9	17·8
1·298	31·7	19·6
1·321	34·7	22·5
1·345	38	23·6

Specific Gravity of Solutions of Sodium Acetate at 17·5°

(*Gerlach*).

Specific Gravity.	Percentage CH_3COONa.	Percentage $CH_3COONa + 3H_2O$.
1·015	3·015	5
1·031	6·030	10
1·047	9·045	15
1·063	12·060	20
1·0795	15·075	25
1·096	18·090	30
1·113	21·105	35
1·1305	24·120	40
1·1485	27·135	45
1·1670	30·150	50

Specific Gravity of Solutions of Chloride of Lime at 15°.

Specific Gravity.	Grams active Chlorine per litre.
1·105	64
1·097	60
1·087	55
1·078	50
1·069	45
1·060	40
1·053	35
1·045	30
1·037	25
1·030	20
1·023	15
1·015	10
1·008	5

Specific Gravity of Solutions of Sulphate of Alumina at 15°.

Specific Gravity.	Percentage $Al_2(SO_4)_3$.	Specific Gravity.	Percentage $Al_2(SO_4)_3$.
1·0170	1	1·1467	14
1·0270	2	1·1574	15
1·0370	3	1·1668	16
1·0470	4	1·1770	17
1·0569	5	1·1876	18
1·0670	6	1·1971	19
1·0768	7	1·2074	20
1·0870	8	1·2168	21
1·0968	9	1·2274	22
1·1071	10	1·2375	23
1·1171	11	1·2473	24
1·1270	12	1·2573	25
1·1369	13		

Specific Gravity of Solutions of Acetate of Alumina at 17°.

Specific Gravity.	Grams Al_2O_3 per litre.
1·100	40·8
1·098	40
1·086	35
1·074	30
1·062	25
1·050	20
1·038	15
1·025	10
1·012	5

Specific Gravity of Solutions of Tartar Emetic at 17·5° (*Streit*).

Specific Gravity.	Percentage Tartar Emetic.	Specific Gravity.	Percentage Tartar Emetic.	Specific Gravity.	Percentage Tartar Emetic.
1·005	0·5	1·015	2·5	1·031	4·5
1·007	1·0	1·018	3·0	1·035	5·0
1·009	1·5	1·022	3·5	1·038	5·5
1·012	2·0	1·027	4·0	1·044	6·0

Specific Gravity of Solutions of Copper Sulphate at 17°.

Specific Gravity.	Percentage $CuSO_4 + 5H_2O$.	Specific Gravity.	Percentage $CuSO_4 + 5H_2O$.
1·0126	2	1·0933	14
1·0254	4	1·1063	16
1·0384	6	1·1208	18
1·0516	8	1·1354	20
1·0649	10	1·1501	22
1·0785	12	1·1659	24

Specific Gravity of Solutions of Chromium Acetate at 17°.

Specific Gravity.	Grams Cr_2O_3 per litre.	Specific Gravity.	Grams Cr_2O_3 per litre.
1·007	5	1·084	60
1·014	10	1·091	65
1·021	15	1·098	70
1·028	20	1·105	75
1·035	25	1·112	80
1·042	30	1·119	85
1·049	35	1·126	90
1·056	40	1·133	95
1·063	45	1·140	100
1·070	50	1·147	105
1·077	55	1·151	107

Specific Gravity of Solutions of Pyrolignite of Iron (Iron Acetate) at 18°.

Specific Gravity.	Grams Fe_2O_3 per litre.	Specific Gravity.	Grams Fe_2O_3 per litre.
1·274	190	1·137	95
1·266	185	1·130	90
1·258	180	1·123	85
1·250	175	1·116	80
1·242	170	1·109	75
1·235	165	1·102	70
1·228	160	1·095	65
1·221	155	1·088	60
1·214	150	1·081	55
1·207	145	1·074	50
1·200	140	1·067	45
1·193	135	1·060	40
1·186	130	1·053	35
1·179	125	1·046	30
1·172	120	1·039	25
1·165	115	1·032	20
1·158	110	1·025	15
1·151	105	1·018	10
1·144	100	1·010	5

Specific Gravity of Solutions of Ferrous Sulphate at 15°.

Specific Gravity.	Percentage $FeSO_4+7H_2O$.	Specific Gravity.	Percentage $FeSO_4+7H_2O$.
1·011	2	1·082	15
1·021	4	1·112	20
1·032	6	1·143	25
1·043	8	1·174	30
1·054	10	1·206	35
1·065	12	1·239	40

Comparative Hydrometer Scale, Sp. Gr., Twaddell, and Baumé, at 12·5° C.

Twaddell.	Baumé.	Specific Gravity.	Twaddell.	Baumé.	Specific Gravity.
0	0	1·000	54	30·6	1·270
1	0·7	1·005	55	31·1	1·275
2	1·4	1·010	56	31·5	1·280
3	2·1	1·015	57	32·0	1·285
4	2·7	1·020	58	32·4	1·290
5	3·4	1·025	59	32·8	1·295
6	4·1	1·030	60	33·3	1·300
7	4·7	1·035	61	33·7	1·305
8	5·4	1·040	62	34·2	1·310
9	6·0	1·045	63	34·6	1·315
10	6·7	1·050	64	35·0	1·320
11	7·4	1·055	65	35·4	1·325
12	8·0	1·060	66	35·8	1·330
13	8·7	1·065	67	36·2	1·335
14	9·4	1·070	68	36·6	1·340
15	10·0	1·075	69	37·0	1·345
16	10·6	1·080	70	37·4	1·350
17	11·2	1·085	71	37·8	1·355
18	11·9	1·090	72	38·2	1·360
19	12·4	1·095	73	38·6	1·365
20	13·0	1·100	74	39·0	1·370
21	13·6	1·105	75	39·4	1·375
22	14·2	1·110	76	39·8	1·380
23	14·9	1·115	77	40·1	1·385
24	15·4	1·120	78	40·5	1·390
25	16·0	1·125	79	40·8	1·395
26	16·5	1·130	80	41·2	1·400
27	17·1	1·135	81	41·6	1·405
28	17·7	1·140	82	42·0	1·410
29	18·3	1·145	83	42·3	1·415
30	18·8	1·150	84	42·7	1·420
31	19·3	1·155	85	43·1	1·425
32	19·8	1·160	86	43·4	1·430
33	20·3	1·165	87	43·8	1·435
34	20·9	1·170	88	44·1	1·440
35	21·4	1·175	89	44·4	1·445
36	22·0	1·180	90	44·8	1·450
37	22·5	1·185	91	45·1	1·455
38	23·0	1·190	92	45·4	1·460
39	23·5	1·195	93	45·8	1·465
40	24·0	1·200	94	46·1	1·470
41	24·5	1·205	95	46·4	1·475
42	25·0	1·210	96	46·8	1·480
43	25·5	1·215	97	47·1	1·485
44	26·0	1·220	98	47·4	1·490
45	26·4	1·225	99	47·8	1·495
46	26·9	1·230	100	48·1	1·500
47	27·4	1·235	101	48·4	1·505
48	27·9	1·240	102	48·7	1·510
49	28·4	1·245	103	49·0	1·515
50	28·8	1·250	104	49·4	1·520
51	29·3	1·255	105	49·7	1·525
52	29·7	1·260	106	50·0	1·530
53	30·2	1·265			

To convert degrees Tw. into sp. gr., multiply by 5, add 1000, and divide by 1000.

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